EXHIBIT D

ANALYTICAL METHODS
FOR PESTICIDES/AROCLORS

Exhibit D - Analytical Methods for Pesticides/Aroclors
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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water, soil, sediment, other solid matrices and oily sludges from hazardous waste sites for the chlorinated pesticides and Aroclors found in the Target Compound List (TCL) in Exhibit C. The method can be used for determining analyte concentrations in the range from the contract required quantitation limits (CRQL) to one million times the CRQL in these matrices when appropriate dilutions are made. The method is based on EPA Method 608, and it covers sample extraction, extract cleanup techniques and GC/EC analytical methods for pesticides and Aroclors.

1.1.2 The target compound list may be designated as all compounds listed in Exhibit C, Pesticide/PCB TCL or a subset of those compounds and will be indicated on the chain of custody accompanying each sample delivery group (SDG).

1.2 Resolution difficulties have been associated with the following pairs of compounds using this method:

- On a DB-608 or equivalent column, DDE and dieldrin; methoxychlor and endrin ketone; and endosulfan I and gamma-Chlordane.
- On a DB-1701 or equivalent column, endosulfan I and gamma-Chlordane, and methoxychlor and endosulfan sulfate.

1.3 There are two isomers of heptachlor epoxide, the endo isomer (isomer A) and the exo isomer (isomer B). The two isomers are separable using current GC capillary columns. Only the exo isomer (isomer B) is of environmental significance. This is the isomer that must be used as an analytical standard, identified and quantitated in sample analysis, and reported on appropriate forms as heptachlor epoxide.

2.0 SUMMARY OF METHOD

2.1 Water Samples

Continuous liquid-liquid or separatory funnel extraction procedures are employed for aqueous samples. A 1 L volume of sample is spiked with the surrogate solution and extracted with methylene chloride using a separatory funnel or a continuous liquid-liquid extractor. The methylene chloride extract is dried with anhydrous sodium sulfate, concentrated and cleaned up by GPC (GPC is required when higher molecular weight compounds are present that interfere with the analyses of target compounds; GPC is optional for all other circumstances). The extract is then solvent-exchanged into hexane, cleaned up by Florisil cartridges, and the final volume adjusted to 1 ml or 2 ml. The extract is analyzed using a dual capillary column Gas Chromatography/Electron Capture Detector (GC/ECD) technique.

2.2 Soil/Sediment/Solid Samples

A 30 g aliquot of sample is spiked with the surrogate solution and then mixed with anhydrous sodium sulfate and extracted with a 1:1 acetone/ methylene chloride solvent mixture by sonication. The extract is filtered, concentrated and solvent-exchanged into methylene chloride. The methylene chloride extract is then cleaned up by GPC (mandatory), solvent-exchanged into hexane, cleaned up by Florisil cartridge, and adjusted to a final volume of 1 ml or 2 ml. The extract is analyzed using a dual capillary column Gas Chromatography/Electron Capture Detector (GC/ECD) technique.

2.3 Oily Sludges (Waste)

A 1 g aliquot of sample is spiked with surrogate solution and quantitatively diluted with methylene chloride. The methylene chloride solution is then cleaned up by GPC (mandatory) and solvent exchanged into hexane. A 1 or 2 ml portion of the solution is cleaned up by Florisil cartridge and the volume is readjusted to 1 or 2 ml. The solution is analyzed by using a dual capillary column Gas Chromatography/Electron Capture Detector (GC/ECD) technique.

2.4 Method Detection Limits

Prior to analysis, method detection limits (MDLs) for all Pesticide compounds in Exhibit C, P/PCB TCL, must be established in accordance with 40 Code of Federal Regulations, Part 136, Appendix B. An MDL study for the PCBs is not required. The MDL study must be reported as detailed in Exhibit B. All MDL values must be less than or equal to one-third of the CRQL. The MDL study must be conducted using the same specifications as for sample analysis. These specifications include but are not limited to: extraction method, initial and continuing calibration conditions and technical acceptance criteria and all instrument operating conditions. The MDL study must be conducted prior to sample analysis, for each alternate column/technique and/or at least annually, whichever, is more frequent. Seven aliquots of reagent water and/or appropriate clean matrix (such as muffled sand) spiked at 3-5 times the expected MDL are analyzed. Separate MDL studies must be conducted for aqueous (either continuous liquid-liquid or separatory funnel extraction) and low level soil/sediment/solid sonication methods. An MDL study is not required for waste dilutions. All sequential analyses of MDL standards must be reported and used in the resulting MDL values which are calculated. The MDL results are calculated as described in 40 CFR, Part 136, Appendix B and reported as a separate SDG in accordance with Exhibit B. The appropriate Students' t value must be clearly provided with the algorithm used to calculate the MDL values. MDLs shall be determined and reported for each instrument/column and method.

The MDL study must be reported as detailed in Exhibit B. The individual analytical sequence raw data must be provided and these data must be summarized in a table which demonstrates the calculated MDL values. The summarized MDL results table must include the concentration found for each compound in each aliquot, the mean concentration of each compound, the percent recovery of each compound, the standard deviation for each compound, and the Method Detection Limit. The true concentration of the

compound in the spike solution must also be provided. The table must list the compounds in the same order as they appear in the target compound list in Exhibit C. In addition, the MDL values for each instrument and method used in reporting results for an SDG shall be submitted with each data package.

The annually determined MDL for an instrument and method shall always be used as the MDL for that instrument/method during that year. If the instrument/method is adjusted in any way that may affect the MDL, the MDL for that instrument/method must be redetermined and the results submitted for use as the established MDL for that instrument/method for the remainder of the year.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the extraction and analysis conditions of the method by running laboratory blanks as defined in Section 12.0. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates which are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures must be used to remove such interferences in order to achieve the contract required quantitation limits.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be made available to all personnel involved in these analyses. Specifically, concentrated sulfuric acid and the 10 N sodium hydroxide solution are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the Aroclors. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this Statement of Work is the responsibility of the Contractor. The Contractor must document in the SDG Narrative when it uses equipment and supplies other than those specified here.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor, Ace Glass Company, Vineland, NJ P/N 6841-10 or equivalent) or Hydrophobic Membrane-based Extractor (Accelerated One Step™ Extractor, Corning series 3195 or equivalent).

6.1.2 Separatory Funnels - 2 L with Teflon stopcock.

6.1.3 Beakers - 400 ml.

6.1.4 Erlenmeyer Flasks - 250 ml.

6.1.5 Syringes - 1 ml, 2 ml or 10 ml (with Luerlok fitting).

6.1.6 Vials and Caps - 20 ml and 10 ml (optional) with screw cap and Teflon or aluminum foil liner, 2 ml capacity for GC auto sampler.

6.1.7 Pipets - glass volumetric 1 ml or 2 ml.

6.1.8 Centrifuge Tube - 12 to 15 ml with 19 mm ground glass joint (optional).

6.1.9 Graduated Cylinder - 1 L capacity.

6.1.10 Drying Column - chromatographic column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts).

6.1.11 Volumetric Flasks - 1 ml, 2 ml and 10 ml.

6.1.12 Bottle or Test Tube - 20 ml with Teflon-lined screw cap for sulfur removal and a glass bottle - 1 L volume, for use in preparation of Bio Beads for packing into column.

6.1.13 Powder Funnels - 10 cm diameter, for filtration/drying.

6.1.14 Buchner Funnels - 9 cm diameter, for filtration.

6.2 Kuderna-Danish (K-D) Apparatus.

6.2.1 Concentrator Tubes - 15 ml and 10 ml graduated (Kontes K-570050-1025 or K-570040-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stoppers are used to prevent evaporation of extracts.

6.2.2 Evaporative Flasks - 500 ml (Kontes K-470001-0500, or equivalent). Attach to concentrator tube with springs.

6.2.3 Snyder Column - three-ball macro (Kontes K-503000-0121, or equivalent).

6.2.4 Snyder Column - two-ball micro (Kontes K-569001 -0219, or equivalent).

6.3 Vacuum System for Eluting Multiple Cleanup Cartridges.

6.3.1 Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.

6.3.2 Vacuum Trap - made from a 500 ml sidearm flask fitted with a one-hole stopper and glass tubing.

6.3.3. Vacuum Pressure Gauge.

6.3.4 Rack for holding 10 ml volumetric flasks in the manifold.

NOTE: Other types of equivalent systems, such as an automated system using syringe pressure, are considered to be acceptable for elution of florisil cartridges, as long as all QC and sample technical acceptance criteria are met.

6.4 pH Paper - wide range (Hydrion Papers, Micro-essential Laboratory, Brooklyn, NY, or equivalent).

6.5 Spatula - stainless steel or Teflon.

6.6 Centrifuge - table top (optional).

6.7 Balances - analytical, capable of accurately weighing ± 0.0001 g, and a top-loading balance capable of weighing 100 g ± 0.01 g. The balances must be calibrated in accordance with ASTM E 617 specifications each 12-hour work shift. The balances must also be annually checked by a certified technician.

6.8 Ultrasonic Cell Disruptor - Heat Systems, Ultrasonics, Inc., Model W-385 (475 watt with pulsing capability, No. 207 3/4-inch tapered disruptor horn) or equivalent device with a minimum 375 watt output capability. NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

6.9 Sonabox Acoustic Enclosure (or equivalent) - for use with disruptor to decrease noise level.

6.10 Ultrasonic Water Bath

6.11 Filter Paper - No. 41 Whatman (or equivalent), 9 cm circles (optional).

6.12 Pyrex Glass Wool - rinsed with methylene chloride and dried before use.

6.13 Silicon Carbide Boiling Chips - approximately 10/40 mesh. Heat to 400 °C for 30 minutes or soxhlet extract with methylene chloride. Teflon Boiling chips rinsed with methylene chloride prior to use are also acceptable.

6.14 Water Bath - heated, with concentric ring cover, capable of temperature control. NOTE: The water bath should be used in a hood.

6.15 GPC Cleanup System

6.15.1 Gel Permeation Chromatography System - GPC Autoprep Model 1002 A or B, Analytical Biochemical Laboratories, Inc., or equivalent. Systems that perform satisfactorily have been assembled from the following components: an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the GPC calibration requirements of Section 10.3.1. NOTE: GPC cleanup is required for extracts for <u>all</u> soil/sediment/solid samples. oily sludges and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target compounds.

6.15.1.1 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) may be attached so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.15.1.2 Guard column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

6.15.1.3 Bio Beads (S-X3) - 200 to 400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 g of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.15.1.4 Ultraviolet detector - fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.15.1.5 Strip chart recorder - recording integrator or laboratory data system.

6.15.1.6 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and 5 micron filter discs or equivalent. Note: Some instrument manufacturer's recommend a smaller micron filter disc. Consult your instrument operation manual to determine the proper size filter disc to use in your system. Check each batch for contaminants by analyzing a GPC blank each time the system is used. Rinse each filter assembly (prior to use) with methylene chloride, if necessary.

6.16 Florisil - 500 mg or 1 g cartridges with stainless steel or Teflon frits, (Catalog No. 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent).

6.17 Nitrogen Evaporation Device - equipped with a heated bath that can be maintained at 35 to 40 °C (N-Evap by Organomation Associates, Inc., South Berlin, MA, or equivalent).

6.18 Oven - drying.

6.19 Desiccator.

6.20 Crucibles - porcelain crucibles or aluminum weighing pans.

6.21 pH Meter - with a combination glass electrode. Calibrate according to manufacturer's instructions. pH meter must be calibrated prior to each use.

6.22 Magnetic Stirrer Motor - Model PC 353, Corning Co., Corning, NY, or equivalent.

6.23 Magnetic Stirrer Bar - Teflon coated, at least 4 cm long.

6.24 Gas Chromatograph/Electron Capture Detector (GC/ECD) System.

6.24.1 Gas Chromatograph - The gas chromatograph (GC) system must be capable of temperature programming and must maintain an optimal flow rate throughout the GC temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases.

6.24.2 Gas chromatographs that are available from some manufacturers may have difficulty in meeting certain method QC requirements because of endrin and DDT breakdown in the injector. This problem can be minimized by operating the injector at 200 - 205 °C, using a Pyrex (not quartz) methyl silicone deactivated injector liner, and deactivating the metal parts in the injector with dichlorodimethyl silane. In some cases, using a packed column injector converted for use with capillary columns may work better than a Grob-type injector. If a Grob-type injector is used, a 4 mm liner may be required to meet breakdown criteria.

6.24.3 Capillary columns - Two fused silica GC columns are required. A separate electron capture detector is required for each column. The specified analytical columns are a 30 meter DB-1701 (J&W Scientific); SPB 1701 (Supelco); AT 1701 (Alltech); RTX-1701 (Restek); CP-Sil 19CB (Chrompack); 007-1701 (Quadrex); BP-10 (SGE); or equivalent, and a 30 meter DB-608 (J&W Scientific); HP-608 (Hewlett Packard); SPB-608 (Supelco); 007-608 (Quadrex); BP-608 (SGE); CP-Sil 8CB (Chrompack); or equivalent. Note that 30 meters is a minimum requirement for

column length. Longer columns may be used as long as they meet all method technical acceptance criteria.

6.24.3.1 The Contractor may choose to use alternate capillary column(s). However, the alternate capillary column(s) selected must meet all the method technical acceptance criteria established in the SOW.

- The GC column must not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (Pesticides/PCBs).
- The GC column must be able to accept concentrations up to the high point standard for individual standard mixtures A and B for each target compound without becoming overloaded.
- The column pair chosen must have dissimilar phases/chemical properties in order to separate the compounds of interest in different RT order.
- The alternate GC column(s) must be used for the entire analysis, including the MDL study, initial and continuing calibration, initial calibration verification and all blank, QC sample and all sample analyses. If a new alternate GC column is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate column. Analytical results generated using this column must meet the technical acceptance criteria listed in the SOW and the CRQLs listed in Exhibit C (Pesticides/PCBs).

6.24.3.2 The alternate GC column must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any column, other than the ones specified in 6.24.3, the Contractor must meet the criteria listed in 6.24.3.1. Once this has been demonstrated, the Contractor must document the column used (brand name, length, diameter, and film thickness) in each SDG Narrative.

6.24.3.3 Manufacturer provided technical information concerning the performance characteristics of the GC column must be included in the MDL Study data package to support the use of the alternate column.

6.24.3.4 A description of the GC columns used for analysis shall be provided in the SDG Narrative.

6.24.3.5 Packed columns must not be used.

6.24.3.6 Columns are mounted in a 0.25-inch injector ports by using glass adapters available from a variety of commercial sources (J&W Scientific, Supelco, Inc., Hewlett-Packard, Varian, Inc., Perkin Elmer, or equivalent). The two columns may be mounted into a single injection port with a tee adapter (Supelco, Inc., Bellefonte, PA, Catalog No. 2-3660, or equivalent). Use of this adapter allows simultaneous injection onto both columns. The laboratory should follow manufacturer's recommendations for mounting capillary columns in injector ports.

6.24.3.7 The carrier gas for routine applications is helium. Laboratories may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative and on all divider pages preceding raw chromatographic data in submissions to the Agency. Laboratories that choose to use hydrogen are advised to exercise caution in its use. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used.

6.24.4 Electron Capture Detector (ECD) - the linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane) or nitrogen according to the instrument specification. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

The GC/EC system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants which may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.24.5 Data System - a data system must be interfaced to the GC/EC. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at the minimum, the output of time vs. intensity (peak height or peak area) data. Also, the data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent Water - defined as water in which an interferent is not observed at or above the CRQL for any target or non-target compound. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb - 300 or equivalent).

7.1.2 Sodium sulfate - granular-anhydrous reagent grade, heated at 400 °C for 4 hours, or at 120 °C for 16 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by GC/ECD to demonstrate that it is free of interference before use. (Baker anhydrous granular, Catalog No. 3375, or equivalent). CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

7.1.3 Concentrated sulfuric acid (H_2SO_4)- 18 N.

7.1.4 Sodium hydroxide solution (NaOH) (10 N) - carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 ml.

7.1.5 10 percent acetone in hexane (v/v) - prepare by adding 10 ml of acetone to 90 ml of hexane. NOTE: Prepare this mixture accurately or the results from the Florisil cartridge cleanup will be adversely affected. Water in the acetone also will adversely affect Florisil performance.

7.1.6 Methylene chloride, hexane, acetone, toluene, iso-octane, and methanol (optional) - pesticide quality or equivalent. It is recommended that each lot of solvent used be analyzed to demonstrate that it is free of interference before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.1.7 Mercury - triple distilled, for sulfur cleanup.

7.1.8 Copper powder (optional) - fine, granular (Mallinckrodt 4649 or equivalent). Copper may be used instead of mercury for sulfur cleanup. Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone, and dry under a steady stream of nitrogen.

7.2 Standards

7.2.1 Standards Documentation

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure described in Exhibit E. The Contractor must be able to verify that the standards are certified by producing the manufacturer's certificates and/or generating the documentation as described in Exhibit E. Manufacturer's certificates of analysis must be retained by the Contractor for the term of the contract. The documentation may be requested during an on-site audit.

7.2.2 Stock standard solutions (1 µg/µL) - may be prepared from pure reference standard materials or may be purchased as certified solutions.

7.2.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene and dilute to volume in a 10 ml volumetric flask with toluene or acetone. Larger wrights/volumes may be used at the convenience of the analyst.

7.2.2.2 When compound purity is assayed to be 97 percent or greater, the weight may be used without correction to calculate the concentration of the stock solution. If the compound purity is

assayed to be less than 97 percent, the weight must be corrected when calculating the concentration of the stock solution. See Exhibit E (Analytical Standards Requirements.)

7.2.2.3 Fresh stock standards must be replaced once every six months after the preparation date (or the date opened for purchased standards). The standards must be replaced sooner if the standards have degraded or concentrated. Stock standards must be checked for signs of degradation or concentration just prior to preparing secondary dilution and working standards from them.

7.2.3 Secondary Dilution Standards

7.2.3.1 Using stock standards, prepare secondary dilution standards in acetone that contain the compounds of interest either singly or mixed together. Secondary dilution standard solutions should be prepared at concentrations that can easily be diluted to prepare working standards.

7.2.3.2 Fresh secondary dilution standards must be prepared once every six months after the preparation date (or the date opened for purchased standards). The standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.4 Working Standards

7.2.4.1 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to all standards, samples, QC samples, and blanks. Prepare a surrogate spiking solution at 0.2 µg/ml for each of the two surrogate compounds in acetone.

7.2.4.2 Matrix Spiking Solution

Prepare a matrix spiking solution in acetone or methanol that contains the following pesticides at the concentrations specified:

Pesticide	Concentration µg/ml
gamma-BHC (Lindane)	0.5
4,4'-DDT	1.0
Endrin	1.0
Heptachlor	0.5
Aldrin	0.5
Dieldrin	1.0

Note: For oily sludge (waste) samples prepared by the waste dilution technique, the matrix spiking solution must be prepared in methylene chloride.

7.2.4.3 GPC Calibration Solution

7.2.4.3.1 Prepare a solution in methylene chloride that contains the following analytes at the minimum concentrations listed below:

Analyte	Concentration mg/ml
Corn oil	25.0
Bis-2-ethylhexyl phthalate	0.5
Methoxychlor	0.1
Perylene	0.02
Sulfur	0.08

7.2.4.3.2 NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.4.4 Florisil Cartridge Check Solution

Prepare a solution of 2,4,5-Trichlorophenol in acetone, at a concentration of 0.1 µg/ml.

7.2.4.5 Resolution Check Mixture

Prepare a mixture in hexane or iso-octane that contains the following pesticides and surrogates at the concentrations listed below.

Compound	Concentration (ng/ml)
gamma-Chlordane	10.0
Endosulfan I	10.0
4,4'-DDE	20.0
Dieldrin	20.0
Endosulfan sulfate	20.0
Endrin ketone	20.0
Methoxychlor	100.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

7.2.4.6 Performance Evaluation Mixture (PEM)

Prepare the PEM in hexane or iso-octane at the concentration levels listed below.

Compound	Concentration (ng/ml)
gamma-BHC	10.0
alpha-BHC	10.0
4,4'-DDT	100.0
beta-BHC	10.0
Endrin	50.0
Methoxychlor	250.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

7.2.4.7 Individual Standard Mixtures A and B

The single component pesticide standards must be prepared in hexane or iso-octane at three concentrations for each analyte, including the surrogates. Two separate calibration mixtures, A and B (listed below), are used to ensure that each peak is adequately resolved. The low point concentration corresponds to the CRQL for each analyte. The midpoint concentration must be 4 times the low point concentration. The high point concentration must be at least 12 times that of the low point (16 times is suggested), but a higher concentration may be chosen by the Contractor. The high point concentration defines the upper end of the concentration range for which the calibration is valid.

Individual Standard Mixture A (INDA) Low Point Concentration	
alpha-BHC	5.0 ng/ml
Heptachlor	5.0 ng/ml
gamma-BHC	5.0 ng/ml
Endosulfan I	5.0 ng/ml
Dieldrin	10.0 ng/ml
Endrin	10.0 ng/ml
4,4'-DDD	10.0 ng/ml
4,4'-DDT	10.0 ng/ml
Methoxychlor	50.0 ng/ml
Tetrachloro-m-xylene	5.0 ng/ml
Decachlorobiphenyl	10.0 ng/ml

Individual Standard Mixture B (INDB) Low Point Concentration	
beta-BHC	5.0 ng/ml
delta-BHC	5.0 ng/ml
Aldrin	5.0 ng/ml
Heptachlor epoxide (exo-epoxy isomer)	5.0 ng/ml
alpha-Chlordane	5.0 ng/ml
gamma-Chlordane	5.0 ng/ml
4,4'-DDE	10.0 ng/ml
Endosulfan sulfate	10.0 ng/ml
Endrin aldehyde	10.0 ng/ml
Endrin ketone	10.0 ng/ml
Endosulfan II	10.0 ng/ml
Tetrachloro-m-xylene	5.0 ng/ml
Decachlorobiphenyl	10.0 ng/ml

NOTE: Only the exo-epoxy isomer (isomer B) of heptachlor epoxide is used as an analytical standard.

7.2.4.8 Multicomponent Standards

Toxaphene and Aroclor standards must be prepared individually except for Aroclor 1260 and Aroclor 1016 which may be combined in one standard mixture. The calibration standards for the Aroclors must be prepared at concentrations of 100 ng/ml, except for Aroclor 1221 which must be prepared at 200 ng/ml. Toxaphene must be prepared at 500 ng/ml. All multicomponent standards must contain the surrogates at 20 ng/ml. The Aroclor and Toxaphene solutions must be prepared in hexane or iso-octane.

7.2.5 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained for 2 years from the manufacturer's preparation date, unless the manufacturer recommends a shorter time period. Standard solutions prepared by the

Contractor which are immediately ampulated in glass vials may be retained for 2 years from the preparation date. Upon breaking the glass seal, the expiration times listed in applicable standard preparation sections will apply. The Contractor is responsible for assuring that the integrity of the standards have not degraded by following proper storage procedures (see Section 7.3).

7.3 Storage of Standard Solutions

7.3.1 Store the stock and secondary dilution standard solutions at 4 °C (± 2 °C) in Teflon-lined screw cap amber bottles/vials. Fresh standards should be replaced or prepared every six months or sooner if comparison with check standards indicates a problem.

7.3.2 Store the working standards at 4 °C (± 2 °C) in Teflon-sealed containers. The solutions should be checked frequently for stability. Working standard solutions must be replaced at the frequency specified above for any particular standard or sooner if comparison with quality control check samples indicates a problem. NOTE: Analysts must allow all standard solutions to equilibrate to room temperature before use.

7.3.3 Refrigeration of the GPC calibration solution may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves.

7.3.4 Samples, sample extracts and standards must be stored separately.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L amber glass containers, fitted with screw-caps lined with Teflon. If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the Region.

8.1.2 If samples are received in containers other than glass, then the Contractor shall contact the RSCC to ascertain the proper procedure for subsampling from the sample container.

8.1.3 All samples must be iced or refrigerated at 4 °C (±2 °C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4 °C (±2 °C) from the time of receipt until 60 days after delivery of a complete, reconciled sample data package to the Agency. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 If sample storage temperatures exceed 4°C (±2 °C) and/or samples are not light protected, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. For all samples that were not properly refrigerated and/or light protected, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG Narrative.

8.2.3 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4 °C (± 2°C) until 365 days after delivery of a complete reconciled data package to the Agency.

8.3.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3.3 Samples, sample extracts, and standards must be stored separately.

8.4 Contract Required Holding Times

8.4.1 Extraction of water samples by separatory funnel procedures must be completed within five days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by continuous liquid-liquid extraction procedures must be started within five days of VTSR. Extraction of soil/sediment/solid samples by sonication must be completed within 10 days of VTSR. Oily sludge (waste) dilutions must be completed within 10 days of VTSR.

8.4.2 As part of the Agency's QA program, the Agency may provide Performance Evaluation samples which the Contractor is required to prepare per the instructions provided by the Agency. The extraction holding time (5 days after VTSR for water and 10 days after VTSR for soil/sediment/ solid samples) does not apply to Performance Evaluation samples. The PE samples must be analyzed and reported with the SDG with which they were submitted.

8.4.3 Extracts of water, soil/sediment/solid samples and oily sludge (waste) samples must be analyzed within 40 days of the start of extraction.

8.4.4 If sample submitted for pesticide/PCB analysis have exceeded contract required holding times and have not yet been extracted and/or analyzed, then the Contractor shall contact the RSCC to ascertain

whether or not the samples should be extracted and/or analyzed. Note that this notification requirement in no way obviates the contractual requirement for the Contractor to extract and/or analyze samples within holding times. If the Contractor is instructed to proceed with extraction and/or analysis outside holding times, sample price may be reduced depending upon the impact of the non-compliance on data usability. For all samples that exceeded holding times, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG narrative.

8.4.5 Pesticide/PCB data reported from sample preparation and/or analyses which were performed outside the contract required holding times for extraction and/or analysis shall be subject to a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Gas Chromatograph Operating Conditions

9.1.1 The following are the gas chromatographic analytical conditions. The conditions are recommended unless otherwise noted.

Carrier Gas:	Helium (hydrogen may be used, see 6.23.3.6)
Column Flow:	1-5 ml/min depending on column ID
Make-up Gas:	P-5/P-10 or N_2 (required)
Injector Temperature:	> 200 °C (see Section 9.1.4)
Injection:	On-column
Injection Volume:	1 or 2 µL (see Section 9.1.3)
Injector:	Grob-type, splitless
Initial Temperature:	150 °C
Initial Hold Time:	0.5 min
Temperature Ramp:	5 C° to 6 C°/min
Final Temperature:	275 °C
Final Hold Time:	Until after decachlorobiphenyl has eluted (approximately 10 minutes)

9.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks and QC samples. The linearity of the ECD may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

9.1.3 Manual injections must be 2 µL. Auto injectors may use 1 µL volumes. The same injection volume must be used for all standards, blanks, samples and QC samples.

9.1.4 Cold (ambient temperature) on-column injectors that allow injection directly onto a column may be used as long as the technical acceptance criteria for resolution, calibration, and analyte breakdown are met.

9.2 Initial Calibration

9.2.1 Summary of Initial Calibration

9.2.1.1 Prior to the analysis of samples, including QC samples and required blanks, each GC/ECD system must be initially calibrated at a minimum of three concentrations to determine instrument sensitivity and the linearity of response utilizing single component target compound and surrogate standards. Multicomponent target compounds are calibrated at a single point concentration at the CRQL.

9.2.1.2 If the technical acceptance criteria for initial calibration are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.2.2 Frequency of Initial Calibration

Each GC/ECD system must be initially calibrated upon award of the contract, whenever major instrument maintenance or modification is performed (e.g., column replacement or repair, cleaning or replacement of ECD, etc.) or if the calibration verification technical acceptance criteria have not been met.

9.2.3 Procedure for Initial Calibration

9.2.3.1 Set up the GC/ECD system as described in Section 9.1

9.2.3.2 Prepare the initial calibration standards using the analytes and the concentrations specified in Section 7.2.4.5 through 7.2.4.8.

9.2.3.3 All standards, samples, QC samples, blanks and extracts must be allowed to warm to ambient temperature before analysis.

9.2.3.4 Analyze the initial calibration sequence as given below. NOTE: Steps 18 and 19 are used as part of the calibration verification as well (see Section 9.3).

INITIAL CALIBRATION SEQUENCE

1. Resolution Check
2. Performance Evaluation Mixture
3. Aroclor 1016/1260
4. Aroclor 1221
5. Aroclor 1232
6. Aroclor 1242
7. Aroclor 1248
8. Aroclor 1254
9. Aroclor 1262
10. Aroclor 1268
11. Toxaphene
12. Low Point Standard A
13. Low Point Standard B
14. Midpoint Standard A
15. Midpoint Standard B
16. High Point Standard A
17. High Point Standard B
18. Instrument Blank
19. Performance Evaluation Mixture

9.2.4 Calculations for Initial Calibration

9.2.4.1 During the initial calibration sequence, absolute retention times (RT) are determined for all single component pesticides, the surrogates, and at least three major peaks of each multicomponent analyte.

9.2.4.2 For single component pesticides, a RT is measured in each of three calibration standards and the mean RT is calculated as the average of the three values. A RT is measured for the surrogates in each of the three analyses of Individual Standard Mixture A during the initial calibration and the mean RT is calculated as the average of the three values. Calculate a mean absolute retention time for each single component pesticide and surrogate using Equation 1.

EQ. 1

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where,

$\overline{RT}$ = Mean absolute retention time of analyte.

RT_i = Absolute retention time of analyte.

n = Number of measurements (3).

9.2.4.3 A retention time window is calculated for each single component analyte and surrogate and for the major peaks (3 to 5) of each multicomponent analyte by using the criteria in Table 1. Windows are centered around the mean absolute retention time for the analyte established during the initial calibrations. Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

9.2.4.4 The linearity of the instrument is determined by calculating a percent relative standard deviation (%RSD) of the calibration factors from the three-point calibration curve for each single component pesticide and surrogate. Either peak area or peak height may be used to calculate calibration factors used in the %RSD equation for each single component pesticide or surrogate. For example, it is permitted to calculate linearity for endrin based on peak area and to calculate linearity for aldrin based on peak height. However, it is not permitted within a %RSD calculation for any particular analyte to use calibration factors calculated from both peak area and peak height. (For example, the calibration factor for the low point standard for endrin cannot be calculated using peak height when the midpoint and high point standard calibration factors for endrin are calculated using peak areas).

9.2.4.5 Calculate the calibration factor for each single component pesticide and surrogate over the initial calibration range using Equation 2. The calibration factors for the surrogates are calculated from the three analyses of Individual Standard Mixture A only.

9.2.4.6 Calculate the mean calibration factor and the %RSD of the calibration factors for each single component pesticide and surrogate over the initial calibration range using Equations 3 and 4.

EQ. 2

$$CF = \frac{Peak\ area\ (or\ height)\ of\ the\ standard}{Mass\ injected\ (ng)}$$

EQ. 3

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

EQ. 4

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

Where,

$$SD_{CF} = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{(n-1)}}$$

$\overline{CF}$ = Mean calibration factor
%RSD = Percent relative standard deviation
SD_{CF} = Standard deviation of calibration factors
CF_i = Individual Calibration factors
n = Total number of values (3)

9.2.4.7 A calibration factor is calculated for each peak in a selected set of three to five major peaks for each multicomponent analyte using Equation 2.

9.2.4.8 Calculate the percent breakdown of DDT, the percent breakdown of endrin and the combined breakdown of DDT and endrin in the PEM using Equations 5, 6, 7 and 8.

EQ. 5

$$Amount\ found\ (ng) = \frac{Peak\ area\ (height)\ of\ compound\ in\ PEM}{CF_{mp}}$$

Where,

CF_{mp} = The calibration factor for the compound determined from the midpoint standard in the most recent initial calibration. NOTE: If during the initial calibration, linearity was determined based on peak area for the compound, then the midpoint CF must be based on peak area. If during the initial calibration, the linearity for the compound was determined based on peak height for the compound, then the midpoint CF must be based on peak height.

EQ. 6

$$\%Breakdown\ DDT = \frac{Amount\ found\ (ng)\ (DDD+DDE)}{Amount\ (ng)\ of\ DDT\ injected} \times 100$$

EQ. 7

$$\%Breakdown\ Endrin = \frac{Amount\ found\ (ng)\ (endrin\ aldehyde + endrin\ ketone)}{Amount\ (ng)\ of\ endrin\ injected} \times 100$$

EQ. 8

$$Combined\ \%Breakdown = \%Breakdown\ DDT + \%Breakdown\ Endrin$$

9.2.4.9 Calculate the concentration (C_{calc}) of each single component pesticide and surrogate in both PEM analyses in the initial calibration sequence (Section 9.2.3.4) using Equation 5. Using the C_{calc}, calculate the percent difference (%D) for each single component pesticide and surrogate in both PEM analyses using Equation 9.

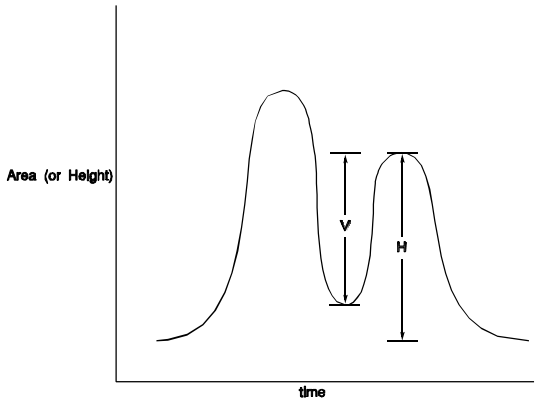
EQ. 9

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100$$

Where,

%D = Percent difference
C_{nom} = Nominal (added) concentration of each analyte
C_{calc} = Calculated concentration of each analyte from the analyses of the PEM standards.

9.2.4.10 Calculate the resolution between each of the analytes in the Resolution Check Mixture, the Performance Evaluation Mixture (both PEMs analyses in the initial calibration sequence), and the midpoint concentration of Individual Standard Mixtures A and B (INDA and INDB) using Equation 10.



EQ.10

$$\%Resolution = \frac{V}{H} \times 100$$

Where,

V = Depth of the valley between the two peaks. The depth of the valley is measured along a vertical line from the level of the apex of the shorter peak to the floor of the valley between the two peaks.
H = Height of the shorter of the adjacent peaks, measured from the baseline.

9.2.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to both GC columns.

9.2.5.1 The initial calibration sequence must be analyzed according to the procedure and in the order listed in Section 9.2.3.4, at the concentrations listed in Sections 7.2.4.5 through 7.2.4.8, and at the frequency listed in Section 9.2.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.

9.2.5.2 The resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0 percent resolved on each column.

9.2.5.3 All single component pesticide and surrogate peaks in both runs of the PEM must be greater than or equal to 90.0 percent resolved on each column.

9.2.5.4 The absolute retention times for each of the single component pesticides and surrogates in both runs of the PEM must be within the retention time windows determined from the three-point initial calibration as described in Section 9.2.4.3.

9.2.5.5 The percent difference of the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in both of the PEM runs of each GC column must be greater than or equal to -25.0 AND less than or equal to +25.0 percent using Equation 9.

9.2.5.6 The percent breakdown of DDT and endrin in each of the PEM runs must be less than or equal to 20.0 percent. Additionally, the combined breakdown of DDT and endrin as calculated using Equation 8 must be less than or equal to 30.0 percent.

9.2.5.7 The %RSD of the calibration factors (CF) for each single component target compound in the initial calibration sequence must be less than or equal to 20.0 percent, except alpha-BHC and delta-BHC. The %RSD of the calibration factors for alpha-BHC and delta-BHC must be less than or equal to 25.0 percent. The %RSD of the calibration factors for the two surrogates must be less than or equal to 30.0 percent. Up to two single component target compounds (but not surrogates) per column may exceed the 20.0 percent limit for %RSD (25.0 percent for alpha-BHC and delta-BHC), but those compounds must have a %RSD of less than or equal to 30.0 percent.

9.2.5.8 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.

9.2.5.9 All instrument blanks must meet the technical acceptance criteria for instrument blanks in Section 12.1.5.4.

9.2.5.10 The identification of single component pesticides by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can only be verified from an on-scale chromatogram. The identification of multicomponent analytes by gas chromatographic methods is based primarily on pattern recognition and on peak retention times displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and multicomponent analytes.

- The chromatograms that result from the analyses of the Resolution Check Mixture, the PEM, and Individual Standard Mixtures A and B during the initial calibration sequence must display the single component analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale.

- The chromatograms for at least one of the three analyses each of Individual Standard Mixtures A and B from the initial calibration sequence must display the single component

analytes at greater than 50 percent and less than 100 percent of full scale.

- The chromatograms of the standards for the multicomponent analytes analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25 percent and less than 100 percent of full scale.

- For any standard containing alpha-BHC, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

- If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

- If the chromatogram of any standard needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

9.2.6 Corrective Action for Initial Calibration

9.2.6.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake out the detector, clean the injection port, or take other corrective actions to achieve the technical acceptance criteria.

9.2.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. In the case of low level contamination, baking out the detector at an elevated temperature (350 °C) should be sufficient to achieve acceptable performance. In the case of heavy contamination, passing hydrogen through the detector for 1-2 hours at an elevated temperature may correct the problem. In the case of severe contamination, the detector may require servicing by the ECD manufacturer. DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.

9.2.6.3 If a laboratory cleans out a detector using an elevated temperature, the ECD electronics must be turned off during the bake out procedure.

9.2.6.4 After bake out or hydrogen reduction, the detector must be recalibrated using the initial calibration sequence (Section 9.2.3.4).

9.2.6.5 Initial calibration technical acceptance criteria must be met before any samples, including QC samples, or required blanks are analyzed. Any samples or required blanks analyzed before the initial calibration technical acceptance criteria have been met will require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.2.6.6 Sample analyses reported with non-compliant initial calibration technical acceptance criteria after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.3 Calibration Verification

9.3.1 Summary of Calibration Verification

Three types of analyses are used to verify the calibration and evaluate instrument performance. The analyses of instrument blanks, PEMs, and the midpoint concentration of Individual Standard Mixtures A and B constitute the continuing calibration. Sample data are not

acceptable unless bracketed by acceptable analyses of instrument blanks, PEMs, and both Individual Standard Mixtures A and B.

9.3.2 Frequency of Calibration Verification

9.3.2.1 An instrument blank and the PEM must bracket one end of a 12-hour period during which sample data are collected, and a second instrument blank and the midpoint concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.

9.3.2.2 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence bracket the front end of the next 12-hour period (Section 9.2.3.4). The injection of the instrument blank starts the beginning of that 12-hour period. Samples may be injected for 12 hours from the injection of the instrument blank. The three injections immediately after the second 12-hour period must be an instrument blank, the midpoint Individual Standard Mixture A, and the midpoint Individual Standard Mixture B. The instrument blank must be analyzed first, before either standard. The Individual Standard Mixtures may be analyzed in either order (A,B or B,A).

9.3.2.3 The analyses of the instrument blank and Individual Standard Mixtures A and B immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the technical acceptance criteria in Section 9.3.5. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixtures fails to meet the technical acceptance criteria in Section 9.3.5 or 72 hours have elapsed. The 12-hour time period <u>always</u> begins with the injection of the instrument blank.

9.3.2.3.1 Standards (PEM or Individual Standard Mixtures), samples QC samples and/or required blanks may be injected for 12 hours from the time of injection of the instrument blank.

9.3.2.4 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and PEM <u>must</u> be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard was injected.

9.3.2.5 The requirements for running the instrument blanks, PEM, and Individual Standard Mixtures A and B are waived when no samples, dilutions, reanalyses, method/sulfur blanks, QC samples, and multicomponent analytes for the 72-hour confirmation requirement are analyzed during that 12-hour period. To resume analysis, using the existing initial calibration curve, the Contractor first must analyze an instrument blank and PEM which must meet their respective technical acceptance criteria before samples may be analyzed.

9.3.2.6 If the entire 12-hour period is not required for the analyses of all samples to be reported, the sequence <u>must</u> be ended with either the instrument blank/PEM combination or the instrument blank/Individual Standard Mixtures A and B combination, whichever was due to be performed at the end of that 12-hour period.

9.3.3 Procedure for Calibration Verification

9.3.3.1 Analyze the PEM, instrument blank and the midpoint concentration of Individual Standard Mixtures A and B at the required frequencies (Section 9.3.2).

9.3.3.2 All standards and blanks must be at ambient temperature at the time of preparation and analysis.

9.3.4 Calculations for Calibration Verification

9.3.4.1 For each analysis of the PEM used to demonstrate continuing calibration, calculate the resolution between the analytes using Equation 10, the concentration (C_{calc}) of each analyte in the PEM using Equation 5 and the percent difference (%D) between the C_{calc} of each analyte (including the surrogates) found in the PEM and the nominal (added) amount (C_{nom}) using Equation 9.

9.3.4.3 Calculate the percent breakdown of DDT and endrin, and the combined breakdown in each PEM analyzed using Equations 5, 6, 7, and 8.

9.3.4.4 For each analysis of the midpoint concentration of INDA and INDB used to demonstrate continuing calibration, calculate the resolution between the analytes using Equation 10, the concentration (C_{calc}) of each analyte in both INDA and INDB using Equation 5 and the percent difference (%D) between the C_{calc} of each analyte (including the surrogates) found in each mixture and the nominal (added) amount (C_{nom}) using Equation 9. Do not attempt to calculate the breakdown of Endrin and DDT in the Individual Standard Mixtures, as these standards contain the breakdown products as well as the parent compounds.

9.3.5 Technical Acceptance Criteria for Calibration Verification

All calibration verification technical acceptance criteria apply independently to each column. Each column must meet the technical acceptance criteria.

9.3.5.1 The PEMs, Individual Standard Mixtures A and B and instrument blanks must be analyzed at the required frequency on a GC/ECD system that has met the initial calibration technical acceptance criteria (Section 9.2.5).

9.3.5.2 All single component pesticides and surrogates in the PEMs used to demonstrate continuing calibration must be greater than or equal to 90.0 percent resolved. The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the continuing calibration must be greater than or equal to 90.0 percent.

9.3.5.3 The absolute retention time for each of the single component pesticides and surrogates in the PEMs and midpoint concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be within the retention time windows determined from the three-point initial calibration in Section 9.2.4.3.

9.3.5.4 The percent difference (%D) between the calculated amount and the nominal amount (amount added) for each of the single component pesticides and surrogates in the PEM must be greater than or equal to -25.0 percent and less than or equal to +25.0 percent.

9.3.5.5 The percent difference (%D) between the calculated amount and the nominal amount (amount added) for each of the single component pesticides and surrogates in the INDA and INDB that have been used as calibration verification must be greater than or equal to -25.0 percent and less than or equal to +25.0 percent.

9.3.5.6 The percent breakdown of DDT in the PEM must be less than or equal to 20.0 percent on each column. The percent breakdown of endrin in the PEM must be less than or equal to 20.0 percent on each column. The combined breakdown of both DDT and endrin must be less than or equal to 30.0 percent on each column.

9.3.5.7 All instrument blanks must meet the technical acceptance criteria in Section 12.1.5.4.

9.3.5.8 The identification of single component pesticides by gas chromatographic methods is based primarily on retention time data. Since the retention time of the apex of a peak can only be verified from an on-scale chromatogram, the following requirements must be met for continuing calibration to be acceptable.

9.3.5.8.1 The chromatograms that result from the analyses of the PEM and the Individual Standard Mixtures must display the single component analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale.

9.3.5.8.2 For any PEM, Individual Standard Mixture or blank, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

9.3.5.8.3 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

9.3.5.8.4 If the chromatogram of any standard or blank needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram(s) must be submitted in the data package.

9.3.6 Corrective Action for Calibration Verification

9.3.6.1 If the technical acceptance criteria for the calibration verification are not met, inspect the system for problems and take the necessary corrective action to achieve the technical acceptance criteria.

9.3.6.2 Major corrective actions such as replacing the GC column or baking out the detector will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.2.5.

9.3.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard (PEM or Individual Standard Mixture) that originally failed the criteria and an associated instrument blank immediately after the corrective action do meet all the technical acceptance criteria.

9.3.6.4 If a PEM or Individual Standard Mixture does not meet technical acceptance criteria listed above, it must be reinjected immediately. If the second injection of the PEM or Individual Standard Mixture meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be run before more sample data are collected.

9.3.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.5.4, all data collection must be stopped. Appropriate corrective action must be taken to clean out the system, and an acceptable instrument blank must be analyzed before more sample data are collected.

9.3.6.6 Analysts are reminded that running an instrument blank and a PEM or Individual Standard Mixtures once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks and standards more often to avoid discarding data.

9.3.6.7 If a successful instrument blank and PEM cannot be run after an interruption in analysis (Section 9.3.2.5), an acceptable initial calibration must be run before sample data may be collected. All acceptable sample analyses must be preceded and followed by compliant standards and instrument blanks, as described in Section 9.3.2.

9.3.6.8 Calibration verification technical acceptance criteria must be met before any samples, including QC samples and required blanks are reported. Any samples, including QC samples and required blanks associated with a calibration verification which did not meet the technical acceptance criteria will require reanalysis at no

additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.3.6.9 Sample results reported with non-compliant calibration verification technical acceptance criteria shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the RSCC to apprise them of the problem. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. All changes in the analyses **must** be preapproved by the Region I Project Officer. The Contractor shall document the Region's decision (including sample weight/volume prepared and analyzed) in the SDG Narrative.

10.1.2 If multiphase samples (e.g., a two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact the RSCC to apprise them of the type of sample received. The RSCC will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do one of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze each phase separately. The RSCC will provide EPA sample numbers for the additional phases.
- Separate the phases and analyze one or more of the phases, but not all of the phases. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do the following:

- Separate the phases and analyze the phase(s) that is amenable to analysis. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other change in the analyses will be permitted. The Contractor shall document the problem, the EPA sample numbers for the affected samples and the Region's instructions in the SDG Narrative.

10.1.3 Extraction of Water Samples

Water samples may be extracted by either a separatory funnel extraction procedure or a continuous liquid-liquid extraction procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction must be employed.

10.1.3.1 Separatory Funnel Extraction

10.1.3.1.1 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder. Measure the pH of each sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Record the pH of the sample "as received" and the exact volume used for extrction on the sample preparation log and on the Form I Pest. Samples requiring pH adjustment must be noted in the SDG Narrative. Transfer the sample into a 2 L separatory funnel.

10.1.3.1.2 Using a syringe or a volumetric pipet, add 1.0 ml of the surrogate standard spiking solution (Section 7.2.4.1) to all water samples.

10.1.3.1.3 Rinse the graduated cylinder with 30 ml of methylene chloride and transfer the rinsate to the separatory funnel. Rinse the

empty 1 L container with 30 ml of methylene chloride and add the rinsate to the separatory funnel. Extract the sample by shaking the funnel for two minutes, with periodic venting to release excess pressure. NOTE: The total volume of solvent used for extraction is 60 ml. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation or other physical means. Drain the methylene chloride layer into a 250 ml Erlenmeyer flask.

10.1.3.1.4 Add a second 60 ml volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Proceed to Section 10.2.

10.1.3.2 Continuous Liquid-Liquid Extraction

10.1.3.2.1 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.2.1.1 Follow manufacturer's instructions for set-up.

10.1.3.2.1.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least one inch above the bottom sidearm.

10.1.3.2.1.3 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure the pH of each sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Record the pH of the sample "as received" and the exact volume used for extraction on the sample preparation log and on the Form I Pest. Samples requiring pH adjustment must be noted in the SDG Narrative. NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.1.4 Using a syringe or volumetric pipet, add 1.0 ml of the surrogate standard spiking solution (Section 7.2.4.1) into the sample and mix well.

10.1.3.2.1.5 Rinse the graduated cylinder with 50 ml of methylene chloride and transfer the rinsate to the continuous extractor. Rinse the empty 1 L container with 50 ml of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.1.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5 to 15 ml/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours. NOTE: When a minimum drip rate of 10-15 mls/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.3.2.1.7 NOTE: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.2.2 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.2.2.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.2.2 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder. Measure the pH of each sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Record the pH of the sample "as received" and the exact volume used for extraction on the sample preparation log and on the Form I Pest. Samples requiring pH adjustment must be noted in the SDG Narrative.

10.1.3.2.2.3 Using a syringe or volumetric pipet, add 1.0 ml of the surrogate standard spiking solution (7.2.4.1) into the sample and mix well.

10.1.3.2.2.4 Rinse the graduated cylinder with 50 ml of methylene chloride and transfer the rinsate to the continuous extractor. Rinse the empty 1 L container with 50 ml of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.2.5 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 ml/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours. (NOTE: Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion which will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to assure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used.) Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.3.2.2.6 NOTE: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane, it may not be necessary to dry the extract with sodium sulfate.

10.1.3.2.3 The contractors may choose to use alternate continuous liquid-liquid extractor types. However, the alternate extractor must be used for all extractions and must meet all the method technical acceptance criteria established in the SOW. If an alternate extractor type is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate extractor. If using alternate extractors or design types, follow the manufacturer's instructions for set-up and operation.

10.1.4 Soil/Sediment/Solid Samples

The "sample" is defined as the entire contents of the sample container. Do not discard any supernatant liquids. Just prior to removing the sample for pH determination, percent moisture analysis and/or extraction, mix the contents of the sample container thoroughly either by gentle shaking or with a narrow metal spatula. Remove and discard any large foreign objects such as sticks, leaves, and rocks in soil samples. For other types of solid materials, break the sample into small soil-like pieces with a metal spatula to increase the surface area.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment/solid to a 100 ml beaker. Add 50 ml of water and continuously stir for 1 hour on a magnetic stirrer. Determine the pH of the sample with a calibrated pH meter while the sample is stirring. Report the pH value on sample preparation logsheets and on the Form I - Pest. If the pH of the

soil/ sediment/solid is greater than 9 or less than 5, document the EPA sample number and the exact pH in the SDG Narrative but do not attempt to adjust the pH of the sample. Discard the portion of sample used to determine the pH. If limited sample volume is received use a smaller 1:1 ratio of grams of soil/sediment/solid sample to mls of reagent water for the pH determination. NOTE: The minimum grams to water ratio for pH determination shall be 5 g to 5 ml. The Contractor must note any deviations to the method in the SDG Narrative.

10.1.4.2 Percent Moisture

10.1.4.2.1 Prior to sample analysis, determine the sample's percent moisture. Weigh 5-10 g of the soil/sediment into a tared crucible and dry overnight or for at least 12 hours in an oven at 105 °C. Allow the sample to cool in a desiccator before reweighing. Calculate the percent moisture using the equation below. Concentrations of individual compounds will be reported relative to the dry weight of soil/sediment/solid.

EQ. 11

$$\%\ Moisture = \frac{grams\ of\ wet\ sample - grams\ of\ dry\ sample}{grams\ of\ wet\ sample} \times 100$$

10.1.4.2.2 If the percent moisture of the sample as determined above is less than 70 percent (< 70%), proceed with extraction and analysis for soil/sediment/solid samples described in Section 10.1.4.

10.1.4.2.3 If the percent moisture of the soil/sediment/solid sample is greater than or equal to 70 percent (≥ 70 %); centrifuge and decant the sample to remove the majority of the water or the sample may be pressure filtered. Determine the percent moisture of the remaining centrifuged/filtered solid sample following Section 10.1.4.2.1 above. If the percent moisture of the centrifuged or filtered soil/sediment/solid sample is less than 70 percent (< 70%), proceed with extraction and analysis of the centrifuged/filtered soil/sediment/solid sample using the soil/sediment/solid sample method described in Section 10.1.4.

10.1.4.2.4 If the percent moisture of the centrifuged/filtered soil/sediment/solid sample is greater than or equal to 70 percent (≥ 70%), then the Contractor shall contact the RSCC for directions. The Region may require that the Contractor do one of the following:

- Analyze the centrifuged/filtered soil/sediment/solid sample "as is";
- Use an additional aliquot (weight) of centrifuged/filtered soil/sediment/solid sample (≥ 70 % M) for extraction and analysis and/or decrease the final extract volume (to no lower than 0.5 ml) to achieve the dry weight CRQLs;
- Use another method of analysis;
- Do not analyze that sample.

10.1.4.2.5 If percent moisture of the centrifuged/filtered soil/sediment/solid sample is greater than 90 percent (> 90%), then the Contractor must contact the RSCC for directions. The Region may require that the Contractor do one of the following:

- Analyze the soil/sediment/solid sample (≥ 90 % M) "as is";

- Use an additional aliquot (weight) of soil/sediment/solid sample (≥ 90 % M) weight for extraction and analysis and/or decrease the final extract volume (to no lower than 0.5 ml) to achieve the dry weight CRQLs;
- Use another method of analysis;
- Do not analyze that sample.

10.1.4.2.6 If a sufficient sample weight/volume has not been provided by the sampler to perform the additional percent moisture determinations and/or to analyze an increased portion of sample, then the Contractor shall contact the RSCC to ascertain whether or not the sample should be analyzed.

10.1.4.2.7 For all samples that do not meet the greater than or equal to seventy percent moisture (≥ 70 %M) requirement, the Contractor shall note the problem, the EPA sample numbers for the affected samples, the initial and subsequent percent moisture(s), and the steps taken to achieve the dry weight CRQLs including the sample weight/ volume prepared and analyzed, the final extract volume and the Region's instructions in the SDG Narrative.

10.1.4.3 Soil/Sediment/Solid Extraction by Sonication

10.1.4.3.1 Tune the sonicator according to the manufacturer's directions prior to extracting samples by this procedure.

10.1.4.3.2 Weigh approximately 30 g of sample to the nearest 0.1 g into a 400 ml beaker and add 60 g of anhydrous powdered or granulated sodium sulfate. Record the exact weight of sample taken on the sample preparation log and the Form I Pest. The sample and the added sodium sulfate should be a homogeneous, granular mixture at this point.

10.1.4.3.3 Add 2.0 ml of the surrogate standard spiking solution (Section 7.2.4.1) to all soil/sediment/solid samples by using a volumetric pipet or a syringe. Immediately add 100 ml of 1:1 methylene chloride-acetone to the sample.

10.1.4.3.4 Place the bottom surface of the sonicator probe about ½ inch below the surface of the solvent but above the sediment layer.

10.1.4.3.5 Sonicate for 3 minutes using a 3/4 inch disruptor horn at full power (output control knob at 10) with pulse on and percent duty cycle knob set at 50 percent. Do <u>not</u> use a microtip. NOTE: These settings refer to the Model W-385. When using a sonicator other then Model W-385, refer to the instructions provided by the manufacturer for appropriate output settings.

10.1.4.3.6 The sample extracts can be gravity or vacuum filtered.

10.1.4.3.7 For gravity filtration prepare a filtration/drying bed by placing a plug of glass wool in the neck of a 10 cm powder funnel and filling the funnel to approximately half its depth (4 or 5 cm) with anhydrous sodium sulfate (80-100 g). Decant the extract through the packed funnel and collect it in a 500 ml evaporative (K-D) flask attached to a concentrator tube.

10.1.4.3.8 For vacuum filtration, use Whatman No. 41 paper in the Buchner funnel. Pre-wet the paper with methylene chloride/acetone before decanting the solvent.

10.1.4.3.9 Repeat the extraction two more times with additional 100 ml portions of the 1:1 methylene chloride-acetone. Before each extraction, thoroughly mix the solid residue and make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula or very carefully, with the tip of the unenergized probe. Decant and filter the extraction solvent after each sonication and combine all three extracts. On the final sonication, pour the entire sample into the funnel and rinse the beaker and

funnel with 60 ml of 1:1 methylene chloride/acetone. Proceed to Section 10.2.

10.1.5 Oily Sludges (Waste)

10.1.5.1 Transfer approximately 1 g (to the nearest 0.1 g) of sample to a to a 20 ml vial which has been precalibrated to 10 ml. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken on the sample preparation log and the Form I Pest. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

10.1.5.2 Add 2.0 g of anhydrous powdered or granulated sodium sulfate to the sample in the vial and mix well. More sodium sulfate may be added to make sure the sample is free-flowing.

10.1.5.3 Surrogates are added to all samples, QC samples and blanks. Add 2.0 ml of the surrogate standard spiking solution (Section 7.2.4.1) to the sample mixture.

10.1.5.4 Immediately dilute to 10 ml with methylene chloride.

10.1.5.5 Cap and sonicate in a sonicator water bath for 2 minutes.

10.1.5.6 Proceed with GPC cleanup (Section 10.3.1).

10.2 Concentrating the Extract

10.2.1 Concentration by K-D

10.2.1.1 Assemble a Kuderna-Danish (K-D) apparatus by attaching a 10 ml concentrator tube to a 500 ml evaporative flask. Other concentration devices or techniques may be used in place of the K-D. If other concentration devices or techniques are used, samples processed using these devices or techniques must meet all the sample technical acceptance criteria established by the SOW.

10.2.1.2 For water sample extracts prepared as described in Section 10.1.3, pour the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and the column with at least two additional 20 to 30 ml portions of methylene chloride to complete the quantitative transfer.

10.2.1.3 Soil/sediment/solid sample extracts prepared by the procedures described in Section 10.1.4 will result in extracts containing a mixture of acetone and methylene chloride. Because all soil/sediment/solid sample extracts MUST be subjected to GPC cleanup prior to analysis, the majority of the acetone must be removed from the extract. The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups. Transfer the extract directly to the K-D concentrator. Rinse the Erlenmeyer flask with 20-30 ml of methylene chloride to complete the quantitative transfer. Transfer the oily sludge extracts directly to the K-D concentrator. Rinse the extraction vial with 20-30 ml of methylene chloride to complete the quantitative transfer.

10.2.1.4 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 ml methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (60 °C to 70 °C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY. Remove the

Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 or 2 ml of methylene chloride.

10.2.1.5 For water extracts which do not require GPC cleanup; proceed with the solvent exchange to hexane described in Section 10.2.2.

10.2.1.6 For water and oily sludge extracts which require GPC cleanup, remove the Snyder column, rinse the flask and its lower joint, collect the rinsate in the concentrator tube, and adjust the volume to 10 ml with methylene chloride. Proceed with GPC cleanup as described in Section 10.3.1.

10.2.1.7 For soil/sediment/solid extracts prepared by the procedure described in Section 10.1.4, it is absolutely necessary to further reduce the volume of the extracts to 1 ml prior to GPC cleanup in order to remove most of the acetone. This is best accomplished using the nitrogen evaporation technique (Section 10.1.7.2). The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups. Finally adjust the 1.0 ml soil/sediment/solid extract volume to 10.0 ml with methylene chloride. Proceed to Section 10.3.1 for mandatory GPC.

10.2.1.8 For all water, soil/sediment/solid or oily sludge extracts which have been through the GPC cleanup step; proceed with the hexane exchange described in Section 10.2.2.

10.2.2 Solvent Exchange into Hexane

This procedure applies to water sample, soil/sediment/solid sample and/or oily sludge sample extracts.

10.2.2.1 With the extract in a K-D apparatus, remove the Snyder column, add 50 ml of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 ml of hexane to the top. Concentrate the solvent extract as described previously (Section 10.1.6.1), but increase the temperature of the water bath (to between 80 and 90 °C recommended). When the apparent volume of liquid reaches 3 to 5 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.2.2 Remove the Snyder column; rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of hexane. Complete the quantitative transfer of the extract to a 10 ml vial by rinsing with hexane.

10.2.2.3 For water samples which have <u>not</u> been subjected to GPC cleanup (Section 10.2.1.5), adjust the final volume of the hexane extract to 10.0 ml. Proceed to Section 10.3.2 for Florisil cartridge cleanup.

10.2.2.4 For water, soil/sediment/solid or oily sludge samples which <u>have</u> been subjected to GPC cleanup, concentrate the hexane extract to 5.0 ml using a micro Snyder column or nitrogen evaporation, as described in Section 10.2.3. Proceed to Section 10.3.2 for Florisil cartridge cleanup.

10.2.3 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before Florisil cleanup or to the final extract volume before instrumental analysis. They are the Micro Snyder Column and Nitrogen Evaporation Techniques.

10.2.3.1 Micro Snyder Column Technique

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 ml of hexane to the top of the column. Place the K-D apparatus in a hot water bath (80 °C to 90 °C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the

apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 0.5 ml, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 ml of hexane. Adjust the final volume with hexane to 1 or 2 ml (see Sample Cleanup by Florisil Cartridge, Section 10.3.2).

10.2.3.2 Nitrogen Evaporation Technique (taken from ASTM Method D 3086)

10.2.3.2.1 Place the concentrator tube in a warm water bath (30 °C to 35 °C recommended) and evaporate the solvent volume to the final volume by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) onto the solvent. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS. Adjust the soil/sediment/ solid extract volume to 10 ml with methylene chloride. Proceed to Section 10.3.1 for mandatory GPC cleanup procedures.

10.2.3.2.2 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or Teflon tubing. Plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal walls of new tubing must be rinsed several times with hexane and then dried prior to use.

10.2.3.2.3 During evaporation, the tube solvent level must be kept below the water level of the bath.

10.3 Cleanup Procedures

There are four cleanup procedures specified in this method: GPC, Florisil cartridge, sulfur and sulfuric acid cleanup. GPC must be performed for all soil/sediment/solid and oily sludge extracts. GPC must be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. Florisil cartridge cleanup is mandatory for all extracts. Sulfur cleanup must be performed for all sample extracts contaminated with sulfur. After the Pest/PCB analysis has been performed, sulfuric acid cleanup must be performed for all extracts which contain, or are suspected to contain, PCBs. Associated blanks and QC samples must be subjected to all the same cleanup(s) procedures as the unspiked samples.

10.3.1 Sample Cleanup by Gel Permeation Chromatography (GPC)

10.3.1.1 Gel Permeation Chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural (and synthetic) macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.3.1.2 GPC Column Preparation

The instructions listed below for GPC column preparation are for Bio Beads. Alternate column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC calibration checks, and 2) the column packings do not introduce contaminants/ artifacts into the sample which interfere with the analysis of the target compounds. Follow the manufacturer's instructions for preparation of the GPC column packing. If alternate column packings are used, samples processed through these packings must meet all the sample technical acceptance criteria established by the SOW.

10.3.1.2.1 Weigh out 70 g of Bio Beads (SX-3). Transfer them to a 1 L bottle with a Teflon-lined cap or a 500 ml separatory funnel

with a large bore stopcock, and add approximately 300 ml of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to cover the beads sufficiently at all times. If a guard column is to be used, repeat the above with 5 g of Bio Beads in a 125 ml bottle or a beaker, using 25 ml of methylene chloride.

10.3.1.2.2 Turn the column upside down from its normal position and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

10.3.1.2.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

10.3.1.2.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a 1 L bottle, quickly transfer it to a 500 ml separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached), and allow the excess solvent to drain. Raise the tube to stop the flow, and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

10.3.1.2.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

10.3.1.2.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat the step in Section 10.3.1.2.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is inserted successfully.

10.3.1.2.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

10.3.1.2.8 Pack the optional 5 cm column with approximately 5 g of pre-swelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

10.3.1.2.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 0.010" ID x 2". Pump methylene chloride through the column at a rate of 5 ml/min for one hour.

10.3.1.2.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as the one in 10.3.1.2.9 above) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not affect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

10.3.1.2.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. The GPC column must be recalibrated after column drying has occurred to verify retention volumes have not changed. NOTE: The description of solvent flow rate and column pressure applies only to the ABC GPC apparatus. Laboratories using equivalent equipment must develop parameters for their apparatus which must meet all GPC technical acceptance criteria.

10.3.1.3 Calibration of GPC

10.3.1.3.1 Summary of GPC Calibration

10.3.1.3.1.1 The GPC calibration procedure is based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.3.1.3.1.2 The UV detector calibration procedure described below is to be used for the analyses of target pesticides and Aroclors listed in Exhibit C.

10.3.1.3.2 Frequency of GPC Calibration

Calibrate the GPC system using the GPC calibration solution prepared as described in Section 7.2.4.3. Each GPC system must be initially calibrated upon award of a contract, when the column is changed, when channeling occurs, when column drying has occurred and once every seven days when samples, including QC samples and blanks are cleaned up using GPC. The Contractor may choose to calibrate the GPC system on a daily basis to ensure appropriate sample collection.

10.3.1.3.3 Procedure for GPC Calibration

The following instructions are for the Analytical Biochemical Laboratories (ABC) system. If you are using a different GPC system, consult the manufacturer's instruction manual for operating instructions. A 2 ml injection loop may be used in place of a 5 ml injection loop in accordance with the manufacturer's instructions.

10.3.1.3.3.1 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 ml (4.5-5.5 ml/min). Once the flow rate is within the required range, record the column pressure (should be 6-10 psi) and room temperature on daily instrument run logs. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored.

10.3.1.3.3.2 Using a 10 ml syringe, load sample loop #1 with calibration solution (Section 7.2.4.3). With the ABC automated system, the 5 ml sample loop requires a minimum of 8 ml of the calibration solution. Use a firm, continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

10.3.1.3.3.3 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace that meets the technical acceptance criteria in Section 10.3.1.3.4. Differences between manufacturer's cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell and, therefore, the analytical flow through detector cell is not acceptable for use.

10.3.1.3.3.4 Using the information from the UV trace, determine the elution times for the phthalate, methoxychlor, and perylene. Phthalate will elute first, perylene, last.

10.3.1.3.3.5 Choose a "DUMP" time which removes > 85 percent of the phthalate. Choose a "COLLECT" time so that > 95 percent of the methoxychlor is collected, and continue to collect until just prior to the elution of sulfur. Use a "WASH" time of 10 minutes.

NOTE: The DUMP and COLLECT times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask. Each laboratory is required to establish its specific time sequences.

10.3.1.3.3.6 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.3.1.3.3.7 Measure the volume of collected GPC eluate in a graduated cylinder and record the volume(s) on the daily instrument log. Changes in the volume of GPC eluate collected for each sample extract processed indicate potential problems with the GPC system during sample processing.

10.3.1.3.3.8 Analyze a GPC blank by loading 5 ml of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using Kuderna-Danish (K-D) evaporator (Section 10.2.1). Exchange the solvent to hexane and analyze the blank extract by GC/ECD according to the procedure in 10.4. Assuming that the blank represents the extract from a 1 L water sample, calculate any detected analyte concentrations using Equation 13.

10.3.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.1.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.3.1.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit > 85 percent resolution.
- Phthalate and methoxychlor peaks must exhibit > 85 percent resolution.
- Methoxychlor and perylene peaks must exhibit > 85 percent resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit > 90 percent baseline resolution.

Percent resolution is calculated using Equation 10 and must be noted on the GPC instrument runlogs.

10.3.1.3.4.2 The solvent flow rate and column pressure must be within the ranges described in Section 10.3.1.3.3.1.

10.3.1.3.4.3 Calculate and record the retention time shifts for bis (2-ethylhexyl) phthalate and perylene between GPC calibrations. The retention time shifts for these two compounds must not vary more than ± 5 percent between calibrations.

10.3.1.3.4.4 The analyte concentrations in the GPC blank must be less than the CRQL of any compound in Exhibit C (Pesticides).

10.3.1.3.4.5 Copies of the UV trace of the calibration solutions and the daily GPC instrument run log must be submitted in the data package with the data for the associated samples.

10.3.1.3.5 Corrective Action for GPC Calibration

10.3.1.3.5.1 If the flow rate and/or column pressure do not fall within the ranges in Section 10.3.1.3.3.1, a new column should be prepared.

10.3.1.3.5.2 If any of the technical acceptance criteria in Section 10.3.1.3.4 cannot be met, the first corrective action step must be to clean the column. The column is cleaned by processing several 5 ml volumes of butylchloride through the system. Butylchloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore the performance of the column, then the column must be repacked with new Bio Beads and recalibrated. It may be necessary to obtain a new lot of Bio Beads if the column continues to fail all GPC technical acceptance criteria.

10.3.1.3.5.3 If the GPC blank is equal to or exceeds the CRQL of any target compound in Exhibit C (Pesticides), pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank as described in Section 10.3.1.3.3.8 to ensure the system is sufficiently clean. If the GPC system still shows signs of contamination, repeat the methylene chloride pumping step until the GPC blank meets the GPC blank technical acceptance criteria (section 10.3.1.3.4.4) or it may be necessary to take the steps outlined in Section 10.3.1.3.5.2 above to clean the column.

10.3.1.3.5.4 If the retention time shifts between the present GPC calibration UV trace and the last GPC calibration UV trace is > 5.0 percent for bis(2-ethylhexyl)phthalate and/or perylene <u>and</u> all other corrective actions fail; then it will be necessary to recalibrate the GPC system as outlined in Section 10.3.1.3.3. Excessive retention time shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.1.4 GPC Calibration Check

10.3.1.4.1 Summary of GPC Calibration Check

The GPC calibration for Pesticide/PCBs must be routinely verified with two check mixtures. No Florisil cleanup is required in the GPC calibration check.

10.3.1.4.2 Frequency of GPC Calibration Check

10.3.1.4.2.1 The GPC calibration check must be performed at least once every 7 days whenever samples, including QC samples, and blanks are cleaned up using the GPC.

10.3.1.4.2.2 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore, system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every seven days. In many cases, the SX-3 Bio Beads may be used for several months as long as the column calibration and flow rate remain constant.

10.3.1.4.3 Procedure for GPC Calibration Check

The instructions below are for a GPC injection loop of 5 ml. If a 2 ml injection loop is used, the Contractor will adjust the extract volume to 4 ml instead of 10 ml before injecting extract on the GPC.

10.3.1.4.3.1 The pesticide GPC calibration check solution contains the following six compounds in methylene chloride: gamma-BHC, Hepatachlor, and Aldrin each at a concentration of 0.1 μg/ml for a 5 ml GPC loop (0.25 μg/ml when a 2 ml GPC loop is used) and 4,4'-DDT, Endrin and Dieldrin at 0.2 μg/ml (0.25 μg/ml for a 2 ml loop). The Aroclor GPC calibration check solution contains 2 μg/ml each of Aroclor 1016 and 1260 in methylene chloride (0.25 μg/ml when a 2 ml GPC loop is used).

10.3.1.4.3.2 Load the first 5 ml sample loop by using a 10 ml syringe containing 8 ml of the pesticide GPC calibration check solution. The Aroclor mixture is loaded into loop #2 in the same manner. A GPC blank (Section 10.3.1.3.3.8) is loaded into loop #3. Fractions are collected in an auto sequence by using the GPC program established by the UV detector calibration procedure (Section 10.3.1.3.3).

10.3.1.4.3.3 Each collected GPC calibration fraction is transferred to a K-D apparatus, and the collection vessel(s) are rinsed with two additional 10 ml portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced according to Section 10.2.1. After cooling, the solvent is exchanged to hexane according to the instructions in Section 10.2.2. The final volume is adjusted to 10 ml, and the sample is analyzed by GC according to the procedure in Section 10.4. The analysis must be performed on only one of the GC columns used for sample analysis.

10.3.1.4.3.4 The pattern of the Aroclor quantitation peaks and the recovery of each single component analyte must be determined for evaluation and reporting purposes.

10.3.1.4.4 Technical Acceptance Criteria for GPC Calibration Check

10.3.1.4.4.1 The GPC must meet the technical acceptance criteria for GPC calibration in Section 10.3.1.3.4 and the GPC calibration must be verified at the frequency listed in Section 10.3.1.4.2.

10.3.1.4.4.2 The recovery of each of the single component analytes must be between 80 - 110 percent.

10.3.1.4.4.3 The Aroclor patterns must be the same as those from the Aroclor 1016 and Aroclor 1260 standards in the initial calibration sequence. Recoveries of the Aroclors must be monitored, extremely low recoveries of the Aroclors would indicate potential problems with the GPC system.

10.3.1.4.5 Corrective Action for GPC Calibration Check

Analysts may continue to use the GPC column if the technical acceptance criteria for the GPC calibration check are met. If the recoveries are out of the acceptance window or if changes in the relative peak heights of the patterns of the Aroclor are observed, the columns must be replaced and the GPC recalibrated according to the instructions in Section 10.3.1.3.1 before

proceeding with any GPC cleanup on samples, including blanks (method and/or sulfur) and QC samples.

10.3.1.5 Sample Cleanup by GPC

10.3.1.5.1 Introduction to Sample Cleanup by GPC

10.3.1.5.1.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could last 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22 °C.

10.3.1.5.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Similarly, extracts containing more than 40 mg/ml of nonvolatile residue must be diluted and loaded into several loops. The nonvolatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or other suitable container. When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected from each run.

10.3.1.5.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is injected onto the column. Viscous extracts, or extracts containing a large amounts of nonvolatile residue, will cause problems with injecting the proper amount of sample extract onto the column using automated injection systems. After the sample extract has been processed, the remaining sample extract in an injection vial must be checked to assure that the proper amount of extract was injected on the column before proceeding with the sample analysis. If the proper amount of extract was not injected, the sample must be re-prepared at no additional cost to the Agency, and the sample extract must either be diluted and loaded into several loops or the sample extract must be injected manually.

10.3.1.5.2 Frequency of Sample Cleanup by GPC

GPC cleanup must be performed at least once for each soil/sediment/solid extract, oily sludge (waste) extract and water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes. In addition, GPC must be performed for all associated blanks and QC samples. If the GPC cleanup procedure is found to be inadequate for the sample matrix, contact the RSCC for instructions.

10.3.1.5.3 Procedure for Sample Cleanup by GPC

10.3.1.5.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 ml syringe. Draw the sample extract through the filter assembly and into the 10 ml syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 ml culture tube with a Teflon-lined screw cap). Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 ml of extract into a 10 ml syringe.

Note: Some GPC instrument manufacturer's recommend using a smaller micron size filter disc. In this instance, follow the manufacturer's recommended operating instructions.

10.3.1.5.3.2 Introduction of particulates or glass wool into the GPC switching valves may require factory repair of the apparatus.

10.3.1.5.3.3 The following instructions are for the Analytical Biochemical Laboratories (ABC) system. If a different GPC system is being used, consult the manufacturer's instruction manual for operating instructions. A 2 ml injection loop may be used in place of a 5 ml injection loop. If a 2 ml injection loop is used, concentrate the sample extract to 4 ml instead of 10 ml and then inject 2 ml instead of 5 ml.

10.3.1.5.3.4 Prior to loading samples, put the GPC into the "load" mode, set the instrument terminal for the number of loops to be loaded, and set the "dump," "collect," and "wash" times for the values determined by the calibration procedure described in Section 10.3.1.3.3.

10.3.1.5.3.5 Using a 10 ml syringe, load the sample into the system. With the ABC automated system, the 5 ml loop requires a minimum of 8 ml of sample. Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5 ml sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi), the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes (this should be done before sample loading). NOTE: Approximately 2 ml of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

10.3.1.5.3.6 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops. After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross contamination. Inject approximately 10 ml of methylene chloride to rinse the common tubes.

10.3.1.5.3.7 After loading all sample loops, index the GPC to the 00 position, switch to the "RUN" mode and start the automated sequence. Process each sample using the collect and dump cycle times established in Section 10.3.1.3.

10.3.1.5.3.8 GPC column pressure and room temperature must be monitored throughout the GPC run. Column pressure and room temperature must be recorded in the GPC instrument log book at the following frequency: Prior to the analysis of the first sample, mid way through sample analysis and after the last sample is collected.

10.3.1.5.3.9 Collect each sample in a 250 ml Erlenmeyer flask covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish evaporator. Sample volumes must be monitored as they are collected and must be consistent with collection volumes established during GPC calibration. Sample volumes must be recorded in the GPC instrument log book. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure.
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.
- Leaks in the system or significant variances in room temperature.

Any discrepancies noted during GPC cleanup and necessary corrective actions must be included in the SDG Narrative.

10.3.1.5.3.10 After the appropriate GPC fraction has been collected for each sample, concentrate the extract as per Section 10.2.1 and proceed to solvent exchange into hexane as described in Section 10.2.2 and Florisil cleanup in 10.3.2.

10.3.1.5.3.11 Any sample extracts that were loaded into two or more GPC loops must be recombined before proceeding with extract concentration.

10.3.2 Florisil Cleanup

10.3.2.1 Introduction

Florisil cartridge cleanup significantly reduces matrix interference caused by polar compounds and is required for all extracts. The same volume of the concentrated extract taken for Florisil cleanup must be maintained after Florisil cleanup (1 or 2 ml).

10.3.2.2 Florisil Cartridge Performance Check

10.3.2.2.1 Summary of Florisil Cartridge Performance Check

Every lot number of Florisil cartridges must be tested before they are used for sample cleanup.

10.3.2.2.2 Frequency of Florisil Cartridge Performance Check

Cartridge performance checks must be conducted at least once on each lot of cartridges prior to use for sample cleanup.

10.3.2.2.3 Procedure for Florisil Cartridge Performance Check

Add 0.5 mL of the Florisil Cartridge Performance Check solution (2,4,5-trichlorophenol, Section 7.2.4.4) and 0.5 mL of Individual Standard Mixture A, (midpoint concentration, Section 7.2.4.7) to 4 mL of hexane. Reduce the final volume to 0.5 mL using nitrogen (Section 10.2.3.2). Place the mixture onto the top of a washed Florisil cartridge, and elute it with 9 mL of hexane/acetone [90:10 V/V]. Use two additional 1 mL hexane rinses to ensure quantitative transfer of standard from the cartridge. Reduce the final volume to 1 mL using nitrogen and analyze the solution by GC/EC using at least one of the GC columns specified for sample analysis. Determine the recovery of each analyte for evaluation and reporting purposes. Calculate the percent recovery (%R) using Equation 12.

EQ. 12

$$Percent\ Recovery = \frac{Q_d}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis
Q_a = Quantity added

10.3.2.2.4 Technical Acceptance Criteria for Florisil Cartridge Performance Check

10.3.2.2.4.1 The cartridge performance check solution must be analyzed on a GC/ECD meeting the initial calibration and calibration verification technical acceptance criteria.

10.3.2.2.4.2 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 120 percent, if the

recovery of trichlorophenol is less than 5 percent, and if no peaks interfering with the target analytes are detected.

10.3.2.2.5 Corrective Action for Florisil Cartridge Performance Check

Any lot of Florisil cartridges that does not meet the technical acceptance criteria above must be discarded and a new lot, which meets all technical acceptance criteria, must be used for sample cleanup.

10.3.2.3 Sample Cleanup by Florisil Cartridge

The required Florisil cartridge size and the final volume of the extract after Florisil cleanup are a function of the GC autosampler that a laboratory uses. If the autosampler operates reliably with 1 mL of sample extract, then a 500 mg cartridge is used and the required final volume is 1 mL. If the autosampler requires more sample, prepare 2 mL of sample extract using a l g cartridge. Manual injection requires only a 1 mL final extract volume and a 500 mg cartridge.

10.3.2.3.1 Frequency of Sample Cleanup by Florisil Cartridge

All sample extracts are required to be cleaned up by the Florisil cartridge technique.

10.3.2.3.2 Procedure for Sample Cleanup by Florisil Cartridge

10.3.2.3.2.1 Attach the vacuum manifold to a water aspirator or to a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5 and 10 pounds of vacuum.

10.3.2.3.2.2 Place one Florisil cartridge into the vacuum manifold for each sample extract.

10.3.2.3.2.3 Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge on the vacuum manifold, by pulling a vacuum, and by passing at least 5 mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.

10.3.2.3.2.4 After the cartridges on the manifold are washed, the vacuum is released, and a rack containing labeled 10 mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.

10.3.2.3.2.5 After the volumetric flasks are in place, the vacuum to the manifold is restored, and a volume of extract equal to the required final volume (1 or 2 mL) from each sample, blank or QC sample extract is transferred to the top frit of the appropriate Florisil cartridge. This volume of extract must equal the final extract volume after Florisil cleanup.

10.3.2.3.2.6 Because the volumes marked on concentrator tubes are not necessarily accurate at the 1 mL level, the use of a syringe or a volumetric pipet is required to transfer the extract to the cleanup cartridge.

10.3.2.3.2.7 The pesticides/Aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/ acetone (90:10) and are collected into the 10 mL volumetric flasks held in the rack inside the vacuum manifold.

10.3.2.3.2.8 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10 mL vial. Use two additional 1 mL

hexane rinses to ensure quantitative transfer of the cartridge eluate.

10.3.2.3.2.9 Adjust the extract to the same 1 or 2 mL aliquot volume as was taken for cleanup using either nitrogen blowdown or a micro Snyder column (Section 10.2.3). Measure the final volume with a syringe or by transferring the extract to a volumetric flask.

10.3.2.3.2.10 If sulfur cleanup is to be performed, proceed to Section 10.2.3. Otherwise, transfer the sample to a GC vial and label the vial. The extract is ready for GC/ECD analysis (Section 10.4).

10.3.3 Sulfur Cleanup

10.3.3.1 Introduction to Sulfur Cleanup

10.3.3.1.1 Sulfur contamination will cause a rise in the baseline of a chromatogram and may interfere with the analyses of the later eluting pesticides. If crystals of sulfur are evident in the sample or sample extract or if the presence of sulfur is suspected, sulfur removal must be performed. Interference which is due to sulfur is not acceptable. Sulfur can be removed by one of the two techniques, detailed below. The Contractor must specify which technique was used on the sample preparation log and in the SDG narrative. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and remove the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

10.3.3.1.2 If only part of a set of samples require sulfur cleanup, then, a sulfur cleanup blank is required for that part of the set.

10.3.3.2 Frequency of Sulfur Cleanup

Sulfur removal is required for all sample and QC sample extracts that contain sulfur.

10.3.3.3 Procedure for Sulfur Cleanup

10.3.3.3.1 Mercury Technique

Add one to three drops of mercury to each hexane extract in a clean vial. Tighten the top on the vial and gently agitate the sample for 30 seconds. Filter or centrifuge the extract. Pipet the extract to another vial and leave all solid precipitate and liquid mercury. If the mercury appears shiny, proceed to Section 10.4 and analyze the extract. If the mercury turns black, repeat sulfur removal as necessary until the mercury appears shiny. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume. CAUTION: Waste containing mercury should be segregated and disposed of properly. NOTE: Mercury is a highly toxic metal and therefore must be used with great care. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

10.3.3.3.2 Copper Technique

Add approximately 2 g of cleaned copper powder to the extract in the centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipet, and transfer the extract to a clean vial. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume. The separation of the extract from the copper powder is necessary to prevent degradation of the

pesticides. If the copper appears bright, proceed to Section 10.4 and analyze the extracts. If the copper changes color, repeat the sulfur removal procedure as necessary until the copper appears bright.

10.3.4 Sulfuric Acid Cleanup

10.3.4.1 Introduction to Sulfuric Acid Cleanup

Pesticide target compounds and other organic compounds can interfere in the identification and quantitation of PCBs. If PCBs are found to be present in the sample after the initial analysis, a portion of the Pest/PCB extract must be sulfuric acid cleaned to improve the identification and quantitation of PCBs.

CAUTION: Sulfuric acid destroys most organic chemicals including many Pesticide target compounds. The acid cleaned sample must be analyzed separately from the Pesticide analysis and in addition to the Pesticide analysis at no additional charge to the Agency.

10.3.4.2 Frequency of Sulfuric Acid Cleanup

Sulfuric acid cleanup is required for all Pest/PCBs extracts which indicate the presence of PCBs after the initial analysis for all target compounds. A portion of the method blank must also be acid cleaned.

10.3.4.3 Procedure for Sulfuric Acid Cleanup

10.3.4.3.1 Using a syringe or a volumetric pipette, transfer 1.0 mL of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5 mL or the 1:1 sulfuric acid solution.

10.3.4.3.2 Cap the vial tightly and shake gently for one minute. CAUTION: Stop immediately if the cap leaks. Sulfuric acid burns skin.

10.3.4.3.3 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored nor should it have a visible emulsion or cloudiness.

10.3.4.3.4 If a clean phase separation is achieved, carefully remove the hexane layer and transfer to a clean 10 mL vial. If not, repeat steps 10.3.4.3.1 through 10.3.4.3.3 with fresh aliquots of sulfuric acid until the hexane extract is no longer colored.

10.3.4.3.5 Add an additional 1 mL of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitative transfer of the PCBs.

10.3.4.3.6 Remove the second hexane layer and combine with the hexane from step 10.3.4.3.4.

10.3.4.3.7 Return the combine extracts to a 1.0 mL final volume using the nitrogen blowdown technique as described in section 10.2.3.2.

10.4 GC/ECD Analysis

10.4.1 Introduction to Sample Analysis by GC/ECD

10.4.1.1 Before samples, QC samples or required blanks can be analyzed, the instrument must meet the initial calibration and calibration verification technical acceptance criteria. Sample analysis on both GC columns is required for <u>all</u> samples, blanks, and QC samples.

10.4.1.2 Sample extracts, standards, QC samples and blanks must be analyzed within an analytical sequence as defined below in Section 10.4.2.1, and under the same GC/ECD instrumental conditions.

10.4.1.3 Set up the GC/ECD system per the requirements in Section 9.0. Unless ambient temperature on-column injection is used (see Section 9.1.4), the injector must be heated to at least 200 °C.

The optimized gas chromatographic conditions as defined in Section 9.1 must be used.

10.4.2 Procedure for Sample Analysis by GC/EC

The injection must be made on-column by using either automatic or manual injection. If autoinjectors are used, 1 µL injection volumes may be used. Manual injections shall use at least 2 µL injection volumes. The same injection volume must be used for all standards, samples, QC samples and blanks associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2 µL. However, the same injection volume must be used for all analyses.

10.4.2.1 Analytical Sequence

All acceptable samples must be analyzed within a valid analytical sequence as given below.

Time	Injection #	Material Injected
	1 - 17	First 17 steps of the initial calibration (Section 9.2.3.4)
0 hr.	18	Instrument blank at end of initial calibration
	19	PEM at end of initial calibration
	20	First sample
	21	
	etc..	Subsequent samples
12 hr.	0	Last sample
	1st injection past 12:00 hr.	Instrument blank
	2nd and 3rd injections past 12:00 hr.	Individual Standard Mixtures A and B
	0	Sample
	etc..	Subsequent samples
Another 12 hr.	0	Last sample
	1st injection past 12 hr.	Instrument blank
	2nd injection	PEM
	0	Sample
	etc...	Subsequent samples
Another 12 hr.	0	Last sample
	1st injection past 12:00 hr.	Instrument blank
	2nd and 3rd injections past 12:00 hr.	Individual Standard Mixtures A and B
	0	Sample
	etc...	Subsequent samples

10.4.2.1.1 NOTE: The first 12 hours are counted from injection #18 (the instrument blank at the end of the initial calibration sequence), not from injection #1. Samples may be injected until 12 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. Because the 12-hour time period is timed from injection of the instrument blank until the injection of the last sample, each 12-hour period may be separated by the length of one chromatographic run, that of the analysis of the last sample. While the 12-hour period may not be exceeded, the laboratory may run instrument blanks and standards more frequently, for instance, to accommodate staff working 8-hour shifts.

10.4.2.1.2 After the initial calibration, the analytical sequence may continue as long as acceptable instrument blanks, PEMs and Individual Standard Mixtures A and B are analyzed at the required frequency. This analytical sequence shows only the minimum required blanks and standards. More blanks and standards may be run at the discretion of the Contractor; these must also satisfy the criteria presented in Section 9 in order to continue the run sequence.

10.4.2.1.3 An analytical sequence must also include all required QC samples and method (and/or sulfur) blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.

10.4.2.1.4 The requirements for the analytical sequence apply to both GC columns and for all instruments used for these analyses.

10.4.3 Procedure for Analysis of Acid Cleaned Samples

Sample extracts originally analyzed for Pesticides and PCBs, which are found to possibly contain PCBs, shall require a sulfuric acid cleanup on a separate portion of the extract. This cleanup removes much of the interference from Pesticides and other organic materials which obscure identification and quantitation of PCBs. The acid cleaned portion of the extract shall be analyzed for PCBs only within a valid 12 hour analytical sequence and quantitated and reported. Report Aroclor results for both the acid cleaned and original extracts on a separate Form 1 Pest using appropriate qualifier flags designated in Exhibit B.

10.5 Sample Dilutions

10.5.1 All samples must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography (defined in Section 11.3).

10.5.2 Use the results of the original analysis to determine the approximate dilution factor required to get the response of the largest analyte peak in the upper half of the initial calibration range of the instrument.

10.5.3 If the response of any single component pesticide is greater than the response of that analyte in the initial calibration high point standard, then the extract must be diluted until the response is within the linear range established during the initial calibration. The chromatographic data from the diluted analysis for any single component pesticide must be able to be reported at greater than 10.0 percent but less than 100.0 percent of full scale.

10.5.4 If the response of the largest peak of any multicomponent analyte is greater than the response of the most intense single component analyte in the initial calibration high point standard; then the sample extract must be diluted to have the response of the largest peak in the multi-component analyte within the linear range of that single component analyte established during the initial calibration. The chromatographic data from the diluted analysis of any multicomponent analyte must be able to be reported at greater than 25.0 percent but less than 100.0 percent of full scale.

10.5.5 If dilution is employed solely to bring a single component peak within the calibration range or to get a multicomponent pattern on scale, then the Contractor must report data for both analyses.

10.5.6 If the Contractor has determined from observation of the sample extract or from previous screening of the sample extract that dilution prior to analysis will be necessary, an undiluted sample analysis may not be required. If an acceptable chromatogram (as defined in Section 11.3) is achieved with the diluted extract, an additional extract 10 times more concentrated than the diluted sample must also be injected and reported with the sample data.

10.5.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram. If the chromatogram of any sample needs to be replotted electronically to meet these requirements both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

10.5.8 Do <u>not</u> submit data for more than two analyses, i.e., the original sample extract and <u>one</u> dilution, or, if a screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

10.5.9 The Contractor may receive instructions with the sampling paperwork which prohibits sample dilutions under any circumstances. This may be required in instances where the CRQLs for most target compounds must be achieved even though one or more target compounds exceed the calibration range and/or high concentrations of non-target compounds are present. In these cases, if screening results indicate that sample dilution is required, then the Contractor shall contact the RSCC to ascertain whether or not that sample should be analyzed at a dilution. For all samples requiring dilutions, the Contractor must note the problem, the EPA sample numbers and any Regional instructions in the SDG Narrative.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The laboratory will identify and quantitate analyte peaks based on the RT windows and the calibration factors (CF) of the midpoint standard (single component pesticides) established during the initial calibration sequence.

11.1.1.2 Analytes are identified when peaks are observed in the RT window for the analyte on both GC columns.

11.1.1.3 Identification of a multicomponent analyte in the sample is based on pattern recognition in conjunction with the elution of three to five sample peaks within the retention time windows of the corresponding peaks of the multicomponent standard on both GC columns. Calibration factors used to quantitate toxaphene and the Aroclors are based on the single-point calibration standard analyzed during the initial calibration. The number of potential quantitation peaks is listed in Table 2.

11.1.1.4 When any multicomponent analyte is detected in a sample, a standard of that multicomponent ananlyte must be run within 72 hours of the analyte's detection (from time of injection), and within a valid 12-hour sequence.

11.1.1.5 The choice of the peaks used for multicomponent analyte identification and the recognition of those peaks may be complicated by the environmental weathering of the toxaphene or Aroclors, and by the presence of co-eluting analytes or matrix interferences, or both. Because of the environmental weathering of these materials, multicomponent analytes in samples may give patterns similar to, but not identical with, those of the standards.

11.1.1.6 If more than one multicomponent analyte is observed in a sample, the Contractor must choose non-common peaks to quantitate each multicomponent analyte. A peak common to both analytes present in the sample must not be used to quantitate either compound.

11.1.2 GC/MS Confirmation of Pesticides and Aroclors

11.1.2.1 Any pesticide or multicomponent analyte listed in Exhibit C for which a concentration is reported from a GC/ECD analysis must have the identification confirmed by GC/MS if the concentration is sufficient for that purpose as defined in Section 11.1.2.3.4, below. The following paragraphs are to be used as guidance in performing GC/MS confirmation. If the Contractor fails to perform GC/MS confirmation as appropriate, the Agency may require reanalysis of any affected samples at no additional cost to the Agency.

11.1.2.2 The GC/MS confirmation may be accomplished by one of three general means:

- Examination of the semivolatile GC/MS library search results (i.e., TIC data), or
- A second analysis of the semivolatile extract, or
- Analysis of the pesticide/Aroclor extract, following any solvent exchange and concentration steps that may be necessary.

11.1.2.3 The semivolatile GC/MS analysis procedures outlined in Exhibit D SVOA are based on the injection into the instrument of approximately 20 ng of a target compound in a 2 µL volume. The semivolatile CRQL values in Exhibit C are based on the sample concentration that corresponds to an extract concentration of 10 ng/µL of target analyte. However, these are quantitation limits, and the detection of analytes and generation of reproducible mass

spectra will routinely be possible at levels 3-10 times lower. The sample concentration corresponding to 10 ng/µL in extract will depend on the sample matrix.

11.1.2.3.1 For water samples, 20 ng/2 µL corresponds to a sample concentration of 10 µg/L.

11.1.2.3.2 For soil/sediment/solid samples prepared according to the semivolatile low level soil/sediment/solid method (i.e., 30 g of soil/sediment), the corresponding sample concentration is 330 µg/Kg.

11.1.2.3.3 For soil/sediment/solid samples prepared according to the semivolatile medium level soil/sediment/solid method (i.e., 1 g of soil/sediment), the corresponding sample concentration is 10,000 µg/Kg.

11.1.2.3.4 Therefore, based on the values given above, any pesticide sample in which the target compound concentration in the sample extract is greater than or equal to 10 ng/µL for single component pesticides, 50 ng/μL for Aroclors, and/or 125 ng/μL for Toxaphene should enable the laboratory to confirm the presence of any pesticide and/or multicomponent analyte by GC/MS analysis of the semivolatile extract.

11.1.2.4 In order to confirm the identification of the target pesticide and/or multicomponent analyte, the laboratory must also analyze a reference standard for that analyte. In order to demonstrate the ability of the GC/MS system to identify the analyte in question, the concentration of the standard should be 10 ng/µL for single component pesticides, 50 ng/μL for Aroclors, and 125 ng/μL for Toxaphene.

11.1.2.5 To facilitate the confirmation of the single component pesticide from the semivolatile library search data, the laboratory may wish to include these analytes in the semivolatile continuing calibration standard at a concentration of 10 ng/µL or less. Do not include any multicomponent analytes in the semivolatile initial or continuing calibration standard. If the single component pesticides are added to this GC/MS standard, the response factors, retention times, etc. for these analytes would be reported on the GC/MS quantitation report, but <u>not</u> on the GC/MS calibration data reporting forms. As only a single concentration of each analyte would be analyzed, no linearity (%RSD) or percent difference criteria would be applied to the response factors for these additional analytes.

11.1.2.6 The laboratory is advised that library search results from the NIST/EPA/NIH (May 1992 release or most recent release) and Wiley (1991 release or most recent release) mass spectral library will not likely list the name of the pesticide/Aroclor analyte as it appears in this SOW, hence, the mass spectral interpretation specialist is advised to compare the CAS Registry numbers for the pesticides/Aroclors to those from the library search routine.

11.1.2.7 If the analyte cannot be confirmed from the semivolatile library search data for the original semivolatile GC/MS analysis, the laboratory may analyze another aliquot of the semivolatile sample extract after further concentration of the aliquot. This second aliquot must either be analyzed as part of a compliant routine semivolatile GC/MS analysis, including GC/MS instrument performance checks (DFTPP), and semivolatile calibration standards containing the single component pesticides as described in Section 11.1.2.5, or it must be analyzed along with separate reference standards for the analytes to be confirmed.

11.1.2.8 If the analyte cannot be confirmed by either the procedures in Sections 11.1.2.5 or 11.1.2.7, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS, following any necessary solvent exchange and concentration steps. As in Section 11.1.2.4, analysis of a reference standard is required if the GC/MS continuing calibration standard does not contain the analyte to be confirmed.

11.1.2.9 Regardless of which of the three approaches described above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the semivolatile extract, then the semivolatile method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the extract prepared for the GC/ECD analysis, then the pesticide method blank extracted with the sample must be analyzed.

11.1.2.10 If the identification of the analyte cannot be confirmed by any of the GC/MS procedures above and the concentration calculated from the GC/ECD analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form I with one of the laboratory-defined qualifiers ("X," "Y," or "Z"). In this instance, list the EPA sample numbers affected, define the qualifier used explicitly in the SDG Narrative, and describe the steps taken to confirm the analyte in the SDG Narrative.

11.1.2.11 For GC/MS confirmation of single component analytes, the required deliverables are copies of the library search results (best TIC matches) or sample analyte spectrum and the spectrum of the reference standard. For multicomponent analytes, spectra of three characteristic peaks are required for both the sample component and the reference standard.

11.1.2.12 The purpose of the GC/MS analysis for the single component pesticides is for identification. The purpose of the GC/MS analysis for the multicomponent analytes is to confirm the presence of chlorinated biphenyls in Aroclor and the presence of chlorinated camphenes in Toxaphene. The GC/MS analytical results for the pesticides/Aroclors shall not be used for quantitation and the GC/MS results shall not be reported on either Form I or Form X. The exception noted in Section 11.1.2.10 applies only to analytes that cannot be confirmed above the reference standard concentration.

11.2 Calculations

11.2.1 Target Compounds

The concentrations of the single component pesticides and surrogates are calculated separately for both GC columns using the following equations.

11.2.1.1 Water

EQ. 13

$$Concentration\ \mu g/L = \frac{(A_x)(V_t)(Df)(GPC)}{(CF)(V_o)(V_i)}$$

Where,

A_x = Area of the peak for the compound to be measured.
CF = Calibration factor from the initial calibration for the midpoint concentration external standard (area per ng).
V_o = Volume of water extracted in milliliters (mL).
V_i = Volume of extract injected in microliters (µL). (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)
V_t = Volume of the concentrated extract in microliters (µL). (If GPC is not performed, then V_t = 10,000 µL. If GPC is performed, then V_t = 5,000 µL.)
Df = Dilution factor. The dilution factor is defined as follows:

$$\frac{\text{µL most concentrated extract + µL clean solvent}}{\text{µL most concentrated extract}}$$

If no dilution is performed, Df = 1.0.

GPC = GPC factor. (If no GPC is performed, GPC = 1. If GPC is performed, then GPC = 2.0)

11.2.1.2 Soil/Sediment/Solid and Oily Sludge (waste)

EQ. 14

$$Concentration\ \mu g/Kg\ (Dry\ weight\ basis) = \frac{(A_x)(V_t)(Df)(GPC)}{(CF)(V_i)(W_s)(D)}$$

Where,

A_x, CF, Df and GPC are as given for water, above.
V_t = 5,000 µL.
V_i = Volume of extract injected in microliters (µL). (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)
$D = \frac{100 - \%\ moisture}{100}$
W_s = Weight of sample extracted in grams (g)

11.2.1.2.1 The GPC factor is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup. Concentrating the extract collected after GPC to 5.0 mL rather than 10.0 mL for water samples not subjected to GPC maintains the sensitivity of the soil/sediment/solid method comparable to that of the water method, but correction of the numerical results is still required.

11.2.1.2.2 Note that the calibration factors used for the quantitation of the single component pesticides are the calibration factors from the midpoint concentration standard in the most recent initial calibration.

11.2.1.2.3 Because of the likelihood that compounds co-eluting with the target compounds will cause positive interferences and increase the concentration determined by the method, the lower of the two concentrations calculated for each single component

pesticide is reported on Form I. In addition, the concentrations calculated for both the GC columns are reported on Form XI, along with a percent difference comparing the two concentrations. The percent difference is calculated according to Equation 15.

EQ. 15

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \times 100$$

Where,

$Conc_H$ = The higher of the two concentrations for the target compound in question

$Conc_L$ = The lower of the two concentrations for the target compound in question

11.2.1.2.4 Note that using this equation will result in percent difference values that are always positive. The value will also be greater than a value calculated using the higher concentration in the denominator; however, given the likelihood of a positive interference raising the concentration determined on one GC column, this is a conservative approach to comparing the two concentrations.

11.2.1.2.5 The quantitative determination of Toxaphene or Aroclors is somewhat different from that of single component pesticides. Quantitation of peaks within the detector linear range CRQL to > 16 times CRQL is based on a single calibration point assuming linear detector response. Alternatively, a linear calibration range may be established during a run sequence by a three-point calibration curve for any multicomponent analyte. If any sample concentration is calculated to be 10^6 times the CRQL, the Contractor shall contact the RSCC immediately.

11.2.1.2.6 The quantitation of Toxaphene or Aroclors must be accomplished by using the heights or the areas of each of the three to five major peaks of the multicomponent analyte in the sample and the calibration factor for the same peaks established during the initial calibration sequence. The concentration of multicomponent analytes is calculated by using Equations 13 and 14, where A_x is the area for each of the major peaks of the multicomponent analyte. The concentration of each peak is determined and then a mean concentration for the three to five major peaks is calculated on each column.

11.2.1.2.7 The reporting requirements for Toxaphene and the Aroclors are similar to those for the single component analytes, except that the lower <u>mean</u> concentration (from three to five peaks) is reported on Form I, and the two mean concentrations reported on Form X. The two mean concentrations are compared by calculating the percent difference using Equation 15.

11.2.2 CRQL Calculation

Sample specific CRQLs must be calculated and reported on Form I Pest. If the adjusted CRQL is less than the CRQL listed in Exhibit C (Pesticides), report the CRQL in Exhibit C (Pesticides).

11.2.2.1 Water Samples

EQ. 16

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(V_x)(V_t)(V_y)(Df)}{(V_o)(V_c)(V_i)}$$

Where,

V_t, Df, V_o, and V_i are as given in equation 13.
V_x = Contract sample volume (1000 mL).
V_y = Contract injection volume (1 µL or 2 µL).
V_c = Contract concentrated extract volume (10,000 µL if GPC was not performed and 5,000 µL if GPC was performed.

11.2.2.2 Soil/Sediment/Solid or Oily Sludge (waste) Samples

EQ. 17

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(W_x)(V_t)(V_y)(Df)}{(W_s)(V_c)(V_i)(D)}$$

Where,

V_t, Df, W_s, V_i and D are as given in equation 14.
W_x = Contract sample weight (30 g soil/sed/solid or 1 g for oily sludge).
V_y = Contract injection volume (1 µL or 2 µL).
V_c = Contract concentrated extract volume (GPC is required: 5000 µL).

11.2.3 Surrogate Recoveries

11.2.3.1 The concentrations of the surrogates are calculated separately for each GC column in a similar manner as the other analytes, using Equations 13 and 14. Use the calibration factors from the midpoint concentration of Individual Standard Mixture A from the initial calibration. The recoveries of the surrogates are calculated for each GC column according to Equation 12.

11.2.3.2 The advisory limits for the recovery of the surrogates are 30 - 150 percent for both surrogate compounds.

11.2.3.3 As these limits are only advisory, no further action is required by the laboratory. However, frequent failures to meet the limits for surrogate recoveries will warrant investigation by the laboratory, and may result in questioning by the Agency. Surrogate recovery data from both GC columns are reported on Form II Pest (see Exhibit B).

11.3 Technical Acceptance Criteria for Sample Analysis

The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

11.3.1 Samples must be analyzed under the GC/ECD operating conditions defined in Section 9.0. The instrument must have met all initial calibration, calibration verification, and blank technical acceptance criteria. Samples must be cleaned-up, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. Samples must be cleaned-up using florisil meeting the technical acceptance criteria for florisil. Samples requiring further clean-up using sulfur or sulfuric acid must meet the respective technical acceptance criteria for sulfur or sulfuric acid. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs and/or Individual Standard Mixtures A and B, as described in Section 10.4.2.1.

11.3.2 The samples must be extracted and analyzed or reextracted and reananlyzed within the contract required holding times defined in Section 8.4.

11.3.3 The samples must have an associated method blank meeting the technical acceptance criteria for method blanks. When sulfur cleanup blanks are required, the samples must have associated with it a sulfur cleanup blank meeting the technical acceptance criteria for sulfur cleanup blanks. When sulfuric acid cleanup blanks are

required, the samples must have associated with it a sulfuric acid cleanup blank meeting the technical acceptance criteria for sulfuric acid cleanup blanks.

11.3.4 The retention time for each of the surrogates must be within the retention time windows as calculated in Section 9.2.4.2 for both GC columns.

11.3.5 No target analyte concentrations may exceed the upper limit of the initial calibration, or else the extract must be diluted and reanalyzed as described in Section 10.5.

11.3.6 A standard for any identified multicomponent analyte must be analyzed during a valid 12 hour analytical sequence on the same instrument and column, within 72 hours of its detection in a sample.

11.3.7 The identification of single component pesticides by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can be verified only from an on-scale chromatogram. The identification of multicomponent analytes is based primarily on pattern recognition and on peak retention times displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and multicomponent analytes.

11.3.7.1 When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses.

11.3.7.2 Chromatograms must display single component pesticides detected in the sample at less than full scale.

11.3.7.3 Chromatograms must display the largest peak of any multicomponent analyte detected in the sample at less than full scale.

11.3.7.4 Chromatograms of any diluted sample extract must display single component pesticides between 10 and 100 percent of full scale.

11.3.7.5 Chromatograms of any diluted sample extract must display the peaks chosen for quantitation of multicomponent analytes between 25 and 100 percent of full scale.

11.3.7.6 For any sample or blank, the baseline of the chromatogram must return to below 50 percent of full scale before the elution time of alpha-BHC, and return to below 25 percent of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

11.3.7.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.3.7.8 If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample analysis technical acceptance criteria MUST be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank or associated cleanup blanks will require re-extraction and reanalysis at no additional cost to the Agency. Any samples analyzed that do not meet the technical acceptance criteria will require re-extraction and/or reanalysis at no additional cost to the Agency. Reextraction and/or reanalysis must be completed within the contract required holding times and must meet all technical acceptance criteria.

11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other

corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reextracted and/or reanalyzed at no additional cost to the Agency after the corrective action.

11.4.3 The extract from samples which were cleaned-up by GPC using an automated injection system and have surrogate recoveries outside the lower advisory surrogate acceptance limits must be checked to assure that the proper amount was injected on the GPC column. If insufficient volume was injected on the GPC, the sample must be reprepared and reanalyzed at no additional cost to the Agency.

11.4.4 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g. carryover, column bleed, dirty ECD, contaminated gasses, leaking septum, etc.). After correcting the problem, analyze an instrument blank to demonstrate that the system is functioning properly. Reanalyze the sample extracts. If the problem with the samples still exists, then those samples must be re-extracted and reanalyzed. Samples which do not meet the given technical acceptance criteria after one re-extraction and three-step cleanup (GPC, Florisil, and sulfur) are then reported in the SDG Narrative by EPA smaple number with a summary of the problem and do not require further analysis.

11.4.5 If the technical acceptance criteria for initial calibration, calibration verification and/or method blanks are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. Any samples analyzed when the above technical acceptance criteria have not been met must be reanalyzed at no additional cost to the agency. Reanalysis must be completed within the contract required holding times and must meet all technical acceptance criteria.

11.4.6 Sample analyses reported with non-compliant initial calibration, calibration verification or method blanks may be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Introduction

There are two types of blanks always required by this method: the method blank and the instrument blank. In addition, several cleanup blanks are required if any particular cleanup is performed. A GPC blank, as described in section 10.3.1.3.3.8, is required for all samples which are cleaned up using GPC. A separate sulfur cleanup blank may be required if all samples associated with a given method blank are subjected to sulfur cleanup. A separate sulfuric acid cleanup blank may be required if any samples associated with a given method blank are found to contain PCBs. Samples that are associated with a GPC blank, sulfur cleanup blank and/or sulfuric acid cleanup blank, are also associated with the method blank with which they were extracted. The method, GPC, sulfur cleanup and sulfuric acid cleanup blanks must meet their respective technical acceptance criteria prior to sample analysis.

12.1.2 Method Blanks

12.1.2.1 Summary of Method Blanks

A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate for soil/sediment/solid and/or oily sludge samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of the samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2.2 Frequency of Method Blanks

A method blank must be extracted once for the following, whichever is most frequent, and analyzed on each GC/EC system used to analyze samples:

- Each SDG (not to exceed 20 field samples), or
- Each matrix within an SDG, or
- Whenever samples are extracted by the same procedure (continuous liquid-liquid extraction, sonication or waste dilution).

12.1.2.3 Procedure for Method Blank Preparation

12.1.2.3.1 For pesticide/Aroclor analyses, a method blank for water samples consists of a 1 L volume of reagent water spiked with 1.0 mL of the surrogate standard spiking solution (Section 7.2.4.1). For soil/sediment/solid samples, the method blank consists of 30 g of sodium sulfate spiked with 2.0 mL of the surrogate standard spiking solution. For oily sludge (waste) samples, a method blank consists of 8.0 mL of methylene chloride spiked with 2.0 mL of the surrogate standard spiking solution.

12.1.2.3.2 Extract, concentrate, cleanup, analyze and report method blanks according to Sections 10.0 and 11.0.

12.1.2.4 Technical Acceptance Criteria for Method Blanks

12.1.2.4.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.1.2.4.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2.2 using the procedures above and in Section 10 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria. Method blanks must undergo cleanup, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. Method blanks must be cleaned-up using Florisil meeting the technical acceptance criteria for Florisil. If any of the samples required sulfur and/or sulfuric acid cleanup, a portion of the method blank must also be cleaned by the respective procedures. Method blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMS, and individual standard mixtures A and B as described in Section 10.4.2.1.

12.1.2.4.3 The concentration of the target compounds (Exhibit C - Pesticides) in the method blank must be less than the CRQL for each target compound.

12.1.2.4.4 The method blank must meet all sample analysis technical acceptance criteria in Section 11.3.

12.1.2.4.5 Surrogate recoveries must fall within the acceptance windows of 30-150%. In the case of the method blank(s), these limits are <u>not</u> advisory.

12.1.2.5 Corrective Action for Method Blanks

12.1.2.5.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.2.5.2 If contamination is a problem, then the source of the contamination must be investigated and appropriate corrective actions must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and sample processing hardware that lead to discrete artifacts and/or elevated baselines be investigated and appropriate corrective actions be taken and documented before further sample analysis. All samples associated with a contaminated method blank must be re-extracted/reanalyzed at no additional cost to the Agency.

12.1.2.5.3 If the surrogate recoveries in the method blank do not meet the recovery limits listed in 12.1.2.4.5, first reanalyze the method blank. If surrogate recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank must be re-extracted and reanalyzed at no additional cost to the Agency.

12.1.2.5.4 If the method blank failed to meet the criteria listed in Sections 12.1.2.4.2 and 12.1.2.4.4, then there is an instrument problem. Correct the instrument problem and reanalyze the method blank.

12.1.2.5.5 If any technical acceptance criteria (Section 12.1.2.4) for blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with non-compliant blanks, then the contractor may receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data useability.

12.1.3 Sulfur Cleanup Blanks

12.1.3.1 Summary of Sulfur Cleanup Blanks

The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and carried through the sulfur cleanup and analysis procedures. The purpose of the sulfur cleanup blank is to determine the levels of contamination associated with the separate sulfur cleanup steps.

12.1.3.2 Frequency of Sulfur Cleanup Blanks

The sulfur cleanup blank is prepared separately when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set which required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then the method blank must be subjected to sulfur cleanup, and no separate sulfur cleanup blank is required.

12.1.3.3 Procedure for Sulfur Cleanup Blank

12.1.3.3.1 The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. The sulfur blank must also contain the surrogates at the same concentrations as the sample extracts (assuming 100.0 percent recovery). Therefore, add 0.1 mL of the surrogate standard spiking solution (Section 7.2.4.1) to 0.9 mL of hexane in a clean vial, or for a sulfur blank with a final volume of 2 mL, add 0.2 mL of the surrogate standard spiking solution to 1.8 mL of hexane in a clean vial.

12.1.3.3.2 Proceed with the sulfur removal (Section 10.3.3.3) using the same technique (mercury or copper) and in the same batch as the samples associated with the blank.

12.1.3.3.3 Analyze the sulfur cleanup blank with associated samples according to Section 10.4. Assuming that the material in the sulfur cleanup blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using the equation in Section 11.2.1.1. Compare the results to the CRQL values for water samples in Exhibit C (Pesticides).

12.1.3.4 Technical Acceptance Criteria For Sulfur Cleanup Blanks

12.1.3.4.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.1.3.4.2 All sulfur cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 using the procedure referenced in Section 12.1.3.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.3.4.3 Sulfur cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixtures A and B, as described in Section 10.4.2.1.

12.1.3.4.4 The concentration of the target compounds (Exhibit C Pesticides) in the sulfur cleanup blank must be less than the CRQL for each target compound.

12.1.3.4.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.

12.1.3.4.6 Surrogate recoveries must fall within the recovery limits of 30-150%. In the case of the sulfur cleanup blank, these limits are not advisory.

12.1.3.5 Corrective Action for Sulfur Cleanup Blanks

12.1.3.5.1 If a sulfur cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.2.3.5.2 If contamination is a problem, then the source of the contamination must be investigated and appropriate corrective action measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and sample processing hardware that lead to discrete artifacts and/or elevated baselines be investigated and appropriate corrective actions be taken and documented before further sample analysis. All samples associated with a contaminated sulfur cleanup blank must be re-extracted/reanalyzed at no additional cost to the Agency.

12.1.3.5.3 If the surrogate recoveries in the sulfur cleanup blank do not meet the acceptance criteria listed in section 12.1.3.4.5, first reananlyze the sulfur cleanup blank. If surrogate recoveries do not meet the acceptance criteria after reanalysis, the sulfur cleanup blank and all samples associated with that sulfur cleanup blank must be re-extracted and reanalyzed at no additional cost to the Agency.

12.1.3.5.4 If the sulfur cleanup blank failed to meet the criteria listed in Section 12.1.3.4.2 and 12.1.3.4.5, then there is an instrument problem. Correct the instrument problem and reanalyze the sulfur cleanup blank.

12.1.3.5.5 If any technical acceptance criteria (Section 12.1.3.4) for sulfur cleanup blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with non-compliant blanks, then the contractor may receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data useability.

12.1.4 Sulfuric Acid Cleanup Blanks

12.1.4.1 Summary of Sulfuric Acid Cleanup Blanks

If PCBs are found to be present in the sample after the initial analysis for target Pesticides, then a portion of the sample extract requires further cleanup with sulfuric acid to improve the identification and quantitation of PCBs. The sulfuric acid cleanup blank is a modified portion of the method blank. A portion of the method blank extract is subjected to the same sulfuric acid cleanup procedure as those samples indicating the presence of PCBs. The sulfuric acid cleanup blank is analyzed and reported along with the acid cleaned sample extracts. The purpose of the sulfuric acid cleanup blank is to determine the levels of contamination associated with the separate sulfuric acid cleanup steps.

12.1.4.2 Frequency of Sulfuric Acid Cleanup Blanks

The sulfuric acid cleanup blank is prepared when any or all of a set of samples extracted together require sulfuric acid cleanup. A method blank is associated with the entire set of samples. The sulfuric acid cleanup blank is associated with the part of the set which required sulfuric acid cleanup.

12.1.4.3 Procedure for Sulfuric Acid Cleanup Blank

12.1.4.3.1 Proceed with the sulfuric acid cleanup (Section 10.3.4.3) using the same technique for both samples and blanks.

12.1.4.3.2 Analyze the sulfuric acid cleanup blank with associated samples according to Section 10.4. Assuming that the material in the sulfuric acid cleanup blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using the equation in Section 11.2.1.1. Compare the results to the CRQL values for water samples in Exhibit C (Pesticides).

12.1.4.4 Technical Acceptance Criteria For Sulfuric Acid Cleanup Blanks

12.1.4.4.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.1.4.4.2 All sulfuric acid cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.4.2 using the procedure referenced in Section 12.1.4.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.4.4.3 Sulfuric acid cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, and appropriate PCB standards as described in Section 10.4.3.

12.1.4.4.4 The concentration of the target PCB compounds (Exhibit C, Pesticides) in the sulfuric acid cleanup blank must be less than the CRQL for each target compound.

12.1.4.4.5 The sulfuric acid cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.

12.1.4.4.6 Surrogate recoveries must fall within the recovery limits of 30-150%. In the case of the sulfuric acid cleanup blank, these limits are not advisory.

12.1.4.5 Corrective Action for Sulfuric Acid Cleanup Blanks

12.1.4.5.1 If a sulfuric acid cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.4.5.2 If contamination is a problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and sample processing hardware that lead to discrete artifacts and/or elevated baselines be investigated and appropriate corrective actions be taken and documented before further sample analysis. The method blank and all samples associated with a contaminated sulfuric acid cleanup blank must be re-cleaned/reanalyzed at no additional cost to the Agency.

12.1.4.5.3 If surrogate recoveries in the sulfuric acid cleanup blank do not meet the recovery limits listed in section 12.1.4.4.5, first reananlyze the sulfuric acid cleanup blank. If the recoveries are not within the limits after reanalysis, an additional portion of the method blank and all samples associated with that sulfuric acid cleanup blank must be re-cleaned and reanalyzed at no additional cost to the Agency.

12.1.4.5.4 If the sulfuric acid cleanup blank failed to meet the technical acceptance criteria listed in 12.1.4.4.2 and 12.1.4.4.5, then there is an instrument problem. Correct the instrument problem and reanalyze the sulfuric acid cleanup blank.

12.1.4.5.5 If any technical acceptance criteria (Section 12.1.4.4) for sulfuric acid cleanup blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with non-compliant blanks, then the contractor may receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data useability.

12.1.5 Instrument Blanks

12.1.5.1 Summary of Instrument Blanks

An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to

determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry over of analytes from standards or highly contaminated samples into other analyses.

12.1.5.2 Frequency of Instrument Blanks

The first analysis in a 12-hour analytical sequence must be an instrument blank. All acceptable sample analyses are to be bracketed by acceptable instrument blanks, as described in Section 10.4.2.l If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an instrument blank must be analyzed to initiate a new 12-hour sequence.

12.1.5.3 Procedure for Instrument Blanks

12.1.5.3.1 Prepare the instrument blank by spiking the surrogates into hexane or iso-octane for a concentration of 20 ng/mL of tetrachloro-m-xylene and decachlorobiphenyl.

12.1.5.3.2 Anayze the instrument blank according to Section 10.4 at the frequency listed in Section 12.1.5.2

12.1.5.3.3 For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of a 1 L water sample and calculate the concentration of each analyte using the equation in Section 11.2.1.1. Compare the results to one-half the CRQL values for water samples in Exhibit C (Pesticides).

12.1.5.4 Technical Acceptance Criteria for Instrument Blanks

12.1.5.4.1 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.5.2 using the procedure in Section 12.1.5.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.5.4.2 The concentration of each of the target analytes (Exhibit C Pesticides) in the instrument blank must be less than 0.5 times the CRQL for that analyte.

12.1.5.4.3 The instrument blank must meet all sample analysis technical acceptance criteria in Section 11.3.

12.1.5.4.4 Surrogate recoveries must fall within the recovery limits of 30-150%. In the case of the method blank(s), these limits are not advisory.

12.1.5.5 Corrective Action for Instrument Blanks

12.1.5.5.1 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows or surrogate recoveries are below 30 %, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were considered suspect as defined by the criteria described above must be reinjected during a valid analytical run sequence at no additional cost to the Agency and must be reported.

12.1.5.5.2 If the surrogate recoveries in the instrument blank do not meet the technical acceptance criteria listed in section 12.1.4.4, first reanalyze the instrument blank. If surrogate recoveries do not meet the acceptance criteria after reanalysis, the instrument blank and all samples associated with that blank must be reanalyzed at no additional cost to the Agency.

12.1.5.5.3 If sample analyses are reported with any non-compliant instrument blanks, then the contractor shall receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data useability.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for pesticide/Aroclor analyses, the Agency has prescribed a mixture of pesticide/Aroclor target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD Analysis

12.2.2.1 A matrix spike and matrix spike duplicate must be extracted and analyzed at least every 20 samples of each matrix. NOTE: There is no differentiation between "low" and "medium" level soil/sediment/ solid samples in this method. Therefore only one soil/sediment/ solid MS/MSD is to be submitted per Sample Delivery Group (SDG). The Agency may require additional MS/MSD analyses, upon Regional request, for which the Contractor will be paid.

12.2.2.2 As a part of the Agency's QA/QC program, aqueous equipment rinsate blanks (field QC) may accompany soil/sediment/solid samples, water samples and/or oily sludge (waste) samples that are delivered to the laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the designated field QC samples.

12.2.2.3 The Contractor shall not perform MS/MSD analysis on any designated Performance Evaluation (PE) samples.

12.2.2.4 If the EPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume to perform an MS/MSD, then the Contractor shall contact the RSCC to ascertain an alternate sample to be used for the MS/MSD analysis. The EPA sample numbers, Regional instructions, and date of contact must be included in the SDG Narrative.

12.2.2.5 If there is insufficient sample volume remaining in any of the samples in an SDG to perform an MS/MSD, the Contractor shall immediately contact the RSCC to inform them of the problem. The Region will either approve that no MS/MSD be performed, or require that a reduced sample weight/aliquot be used for the unspiked and/or MS/MSD analyses. The RSCC will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.6 The Contractor will not be paid for MS/MSD analyses performed at a greater frequency than required by the contract unless it is requested by the Agency. If the Contractor has a question regarding the frequency, etc., of the MS/MSD analyses for a particular SDG, contact the RSCC for clarification.

12.2.2.7 When a Contractor receives only performance evaluation (PE) samples, no MS/MSD shall be performed within that SDG.

12.2.2.8 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD when the Region did not designate samples to be used for this purpose. If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water Samples

For water samples, measure out two additional 1 L aliquots of the sample chosen for spiking. Adjust the pH of the samples (if required) and fortify each with 1.0 mL of matrix spiking solution (Section 7.2.4.2). Using a syringe or volumetric pipet, add 1.0 mL of surrogate standard spiking solution (Section 7.2.4.1) to each sample. Extract, concentrate, cleanup, and analyze matrix spikes and matrix spike duplicate according to procedures for water samples in Section 10.1.3.

12.2.3.2 Soil/Sediment/Solid Samples

For soil/sediment/solid samples weigh out two additional 30 g (record weight to the nearest 0.1 g) aliquots of the sample chosen for spiking. Add 60 g of anhydrous powdered sodium sulfate to each aliqout. Mix well. Add 1.0 mL of matrix spiking solution (Section 7.2.4.1) and 2.0 mL of surrogate standard spiking solution (Sectin 7.2.4.2). Extract, concentrate, cleanup, and analyze matrix spikes and matrix spike duplicates according to procedures for soil/ sediment/solid samples in Section 10.1.4.

12.2.3.3 Note: Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do not further dilute the MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

12.2.3.4 Oily Sludge Samples - Waste Dilution

For oily sludge (waste) samples, prepare two additional 1 g aliquots (record weight to the nearest 0.1 g) of the sample chosen

for spiking in two precalibrated 20 mL vials. Add 2.0 g of anhydrous powdered sodium sulfate to each aliquot. Mix well. Add 2.0 mL of surrogate standard spiking solution (Section 7.2.4.1) and 1.0 mL of matrix spiking solution (Section 7.2.4.2). Dilute to 10 mL with methylene chloride. Extract, concentrate, cleanup and analyze the MS/MSD according to procedures for oily sludge in Section 10.1.5.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the matrix spike compounds using the same equations used to calculate target compounds (Section 11.2.1).

12.2.4.2 The percent recoveries and the relative percent difference between the recoveries of each of the compounds in the matrix spike samples will be calculated and reported by using the following equations:

EQ. 18

$$Matrix\ Spike\ Recovery = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike sample result
SR = Sample result
SA = Spike added

EQ. 19

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR= Matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.2.5.2 All MS/MSD must be prepared and analyzed at the frequency described in Section 12.2.2 using the procedure above on a GC/ECD system meeting the initial calibration, calibration verification, and blank technical acceptance criteria. MS/MSD must be cleaned-up, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. MS/MSD must be cleaned-up using florisil meeting the technical acceptance criteria for florisil. If necessary, the MS/MSD must also be cleaned-up using sulfur and/or sulfuric acid meeting the technical acceptance criteira for sulfur and/or sulfuric acid. MS/MSD must be brackted at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMS, and individual standard mixtures A and B as described in Section 10.4.2.1.

12.2.5.3 The MS/MSDs must meet all applicable sample analysis technical acceptance criteria as defined in Section 11.3.

12.2.5.4 The technical acceptance criteria for MS/MSD compound recoveries and RPD are given in Table 8. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from the Agency.

12.2.5.5 The MS/MSDs must be extracted and analyzed or reextracted and reananlyzed within the contract holding time specified in Section 8.3.

12.2.5.6 The retention time for each of the surrogates must be within the retention time window as calculated in Section 9.2.4.2 for both GC columns.

12.2.5.7 The limits for matrix spike compound recoveries and RPD are given in Table 3. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet recovery limits or RPD warrant investigation by the laboratory, and may result in questions from the Agency.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria for MS/MSD must be reanalyzed at no additional cost to the Agency. Both sets of data must be reported.

12.2.6.1 Corrective actions for failure to meet GC/ECD initial calibration and calibration verification technical acceptance criteira must be completed before the analysis of any QC samples.

12.2.6.2 Corrective actions for failure to meet blank technical acceptance criteria must be met before the analysis of any QC samples.

12.2.6.3 Corrective actions for failure to meet cleanup technical acceptance criteria must be met before the analysis of any QC samples.

12.2.6.4 If the technical acceptance criteria for MS/MSD analysis are not met, the contractor shall determine whether the non-compliance is due to the sample matrix or GC/ECD system problems.

12.2.6.5 If the non-compliance is found to be due to a sample matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If surrogate recoveries or internal standard compound responses in a sample used for a matrix spike or matrix spike duplicate were outside the technical acceptance criteria, then it should be reanalyzed only if the surrogate recoveries and internal standard compound responses met acceptance criteria in both the matrix spike and matrix spike duplicate analyses.

- If the MS/MSD recoveries/RPD meet the MS/MSD technical acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. The contractor should make every effort to reanalyze the sample within the contract required holding times. If the reanalysis was performed within holding times, then submit data only from the reanalysis. If the reanalysis was performed outside holding times, then submit both sets of data.

- If the MS/MSD recoveries/RPD fail to meet the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B.

12.3 SDG-Specific Performance Evaluation (PE) Samples (PEs)

12.3.1 Summary of-SDG Specific PE Samples

The Region I Performance Evaluation (PE) program has two functions, (1) to evaluate laboratory operation and protocols over a period of

time, and (2) to provide information on the quality of individual data packages.

12.3.2 Frequency of SDG-Specific PE Samples

12.3.2.1 The Region will submit PE samples with every SDG per parameter and matrix (as available). The Region may obtain these SDG Specific PE samples from either a commercial vendor or from the CLP National Program Office (NPO) which provides PE samples in support of the Superfund program. PE samples provided by the CLP-NPO are referred to as "EPA generated".

12.3.2.2 When the Region submits aqueous trip and/or equipment blanks and/or Performance Evaluation samples (PEs) with soil/sediment/solid field samples, then the Contractor shall not perform an MS/MSD analysis on the aqueous matrix (trip blank, equipment blank, PE sample). When the Region submits an aqueous PE sample with aqueous field samples, then the Contractor shall not choose the PE sample for MS/MSD analysis.

12.3.2.3 If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.3.3 Procedure for Preparing SDG-Specific PE Samples

12.3.3.1 Instructions for preparation of the PE samples will be included with each submission of samples.

12.3.3.2 If PE sample directions do not apply to a PE sample received, then the Contractor must contact the RSCC to ascertain whether or not to analyze the PE sample and to obtain appropriate PE sample directions.

12.3.4 Calculations for SDG-Specific PE Samples

12.3.4.1 For EPA generated and commercially prepared PE samples that are submitted with each SDG, the Contractor must correctly identify and quantitate all compounds detected in the PE sample using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.3.5 Technical Acceptance Criteria for SDG-Specific PE Samples

12.3.5.1 All SDG Specific PE samples must be analyzed under the same GC/ECD conditions set up in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.3.5.2 EPA-generated PE samples included with the SDG will be evaluated by the Region using a CLP NPO computer program called PEAC TOOLs. PEAC TOOLs rates the PE sample results based on statistically generated confidence intervals.

12.3.5.3 The results of commercially prepared PE samples will be evaluated using the vendors' statistically generated confidence intervals.

12.3.5.4 Contractor's results on the SDG-Specific PE samples will be evaluated using the most recent Regional PE sample data validation criteria.

12.3.5.5 At a minimum, the PE results will be evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the scores on any given laboratory evaluation sample to compensate for unanticipated difficulties with a particular sample.

12.3.6 Corrective Action for SDG-Specific PE Samples

12.3.6.1 The corrective actions for PE sample results which do not meet the technical acceptance criteria defined in Section 12.3.5.1 above are the same corrective actions outlined for sample analysis in Section 11.4.

12.3.6.2 If a SDG-Specific PE sample evaluated as described in Sections 12.3.5.2 through 12.3.5.6 above, indicates unacceptable laboratory performance then the contractor may be required to reanalyze all samples, standards and QC samples associated with the unacceptable PE sample result (if sufficient volume remains) and/or analyze a new PE sample at no additional cost to the Agency. Unacceptable laboratory performance includes either a TCL false positive result, false negative result, and/or compound misquantitation (reported result exceeds $\pm$ 3 sigma of the spiked compound concentration).

12.3.6.3 SDG-Specific sample results reported with unacceptable PE results shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.4 CLP Quarterly Blind (QB) Laboratory Evaluation Program

12.4.1 Summary of CLP QB Samples

The Region will also submit quarterly laboratory evaluation samples for specified analyses in conjunction with the CLP Quarterly Blind (QB) program. The results from the analysis of these QB samples will be used by the Region to verify the Contractor's continuing ability to produce acceptable analytical data. The results will also be used to assess the precision and accuracy of the analytical methods for specific analytes.

12.4.2 Frequency of CLP QB Samples

12.4.2.1 The Region will submit laboraotry evaluation samples on a quarterly basis for specified analyses in conjunction with the CLP Quarterly Blind (QB) program.

12.4.2.2 If the contractor receives a QB sample without any field samples, no MS/MSD analysis shall be performed with that SDG.

12.4.3 Procedure for Preparing CLP QB Samples

12.4.3.1 Instructions for preparation of the QB samples will be included with each submission of samples.

12.4.4 Calculations for CLP QB Samples

12.4.4.1 The Contractor must correctly identify and quantitate all TCL compounds detected in the QB sample using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.4.5 Technical Acceptance Criteria for CLP QB Samples

12.4.5.1 The QB samples must be analyzed under the same GC/ECD conditions set up in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.4.5.2 The QB samples will be scored and the results will be used to assess the precision and accuracy of the analytical methods for specific analytes.

12.4.5.3 At a minimum, the results are evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the scores on any given laboratory evaluation sample to compensate for unanticipated difficulties with a particular sample.

12.4.5.4 The Contractor's performance on the QB samples will be measured and reported as follows:

12.4.5.4.1 Acceptable, No Response Required (Score greater than or equal to 90%): Data meets most or all of the scoring criteria.

12.4.5.4.2 Acceptable, Response Required Explaining Deficiency(ies) Required (Score greater than or equal to 75% but less than 90%): Deficiencies exist in the Contractor's performance.

12.4.5.4.3 Unacceptable Performance (Score less than 75%): Deficiencies exist in the Contractor's performance to the extent that the National Program Office has determined that the Contractor has not demonstrated the capability to meet the contract requirements.

12.4.5.4.4 In the case of Sections 12.4.5.4.2 and 12.4.5.4.3 above, the Contractor shall respond to the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the Contractor Officer and the Project Officer, within 14 days of receipt of notification from the Agency.

12.4.6 Corrective Action for CLP QB Samples

12.4.6.1 The corrective actions for QB sample results which do not meet the technical acceptance criteria defined in Section 12.4.5.1 above are the same corrective actions outlined for sample analysis in Section 11.4.

12.4.6.2 After receipt and review of the Contractor's deficiency letter (Section 12.4.5.4.4), the Technical Project Officer, Administrative Project Officer, or Contracting Officer will nofity the Contractor concerning the remedy for their unacceptable performance. The Contractor may expect, but the Agency is not limited to, the following actions: commensurate reduction in sample price, zero payment due to data rejection, reduction of the number of samples sent under the contract, suspension of sample shipment to the Contractor, a data package audit, an on-site laboratory evaluation, a remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

NOTE: The Contractor's prompt response demonstrating that corrective actions have been taken to ensure the Contractor's capability to meet contract requirements may facilitate continuation of sample scheduling.

12.4.6.4 If the Contractor fails to adhere to the requirements listed in Section 8 (Exhibit E) and summarized above, the Contractor may expect, but the Agency is not limited to, the following actions: commensurate reduction in sample price, zero payment due to data rejection, reduction in the number of samples sent under the contract, suspension of sample shipment to the Contractor, a data package audit, an on-site laboratory evaluation, a remedial laboratory evaluation sample and/or contract sanctions, such as a Cure Notice.

13.0 METHOD PERFORMANCE

Not Applicable

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16.0 REFERENCES

16.1 U. S. EPA, "USEPA Contract Laboratory Program, Statement of Work for Organic Analyses," OLM03.1, Office of Solid Waste and Emergency response, EPA-540/R-94/073, August, 1994.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Retention Time Windows for Single and Multicomponent Analytes and Surrogates

Compound	Retention Time Window (minutes)
alpha-BHC	± 0.05
beta-BHC	± 0.05
gamma-BHC (Lindane)	± 0.05
delta-BHC	± 0.05
Heptachlor	± 0.05
Aldrin	± 0.05
alpha-Chlordane	± 0.07
gamma-Chlordane	± 0.07
Heptachlor epoxide	± 0.07
Dieldrin	± 0.07
Endrin	± 0.07
Endrin aldehyde	± 0.07
Endrin ketone	± 0.07
4,4'-DDD	± 0.07
4,4'-DDE	± 0.07
4,4'-DDT	± 0.07
Endosulfan I	± 0.07
Endosulfan II	± 0.07
Endosulfan sulfate	± 0.07
Methoxychlor	± 0.07
Aroclors	± 0.07
Toxaphene	± 0.07
Tetrachloro-m-xylene	± 0.05
Decachlorobiphenyl	± 0.10

Table 2

Number of Potential Quantitation Peaks

Multicomponent Analyte	No. of Potential Quantitation Peaks
Aroclor 1016/1260	5/5
Aroclor 1221	3
Aroclor 1232	4
Aroclor 1242	5
Aroclor 1248	5
Aroclor 1254	5
Aroclor 1262	5
Aroclor 1268	5
Toxaphene	4

Table 3

Matrix Spike Recovery and Relative Percent Difference Limits

Compound	%Recovery Water	RPD Water	%Recovery All Solid Matrices	RPD All Solid Matrices
gamma-BHC (Lindane)	56-123	15	46-127	50
Heptachlor	40-131	20	35-130	31
Aldrin	40-120	22	34-132	43
Dieldrin	52-126	18	31-134	38
Endrin	56-121	21	42-139	45
4,4'-DDT	38-127	27	23-134	50